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INTRODUCTION

Experimental determination of the fiber orientation is a subject of great importance for sheet materials such as paper sheets, nonwoven fabrics, and biomembranes, since it is indispensable in understanding the relationship between the sheet structure and the properties of the sheet materials. It is well known that the orientation of fibers plays an important role in characteristic properties of the sheets such as the mechanical breaking strength and the dimensional stability concerning thermal deformation and humidity expansion.^{8, 11} The molecular or fiber orientation has been investigated by several methods such as X-ray diffraction,^{13, 41, 48, 49} ultrasonic velocity,⁴⁸ mechanical breaking strength,^{4, 11, 39} Young's modulus,^{6, 48} polarized fluorescence,²² laser light,^{2, 42, 43} nuclear magnetic resonance,^{28, 49} soft X-ray radiogram,^{53, 54} and optical or electron microscope.^{2, 10, 20, 40} These conventional methods, however, have some disadvantages to determine the orientation of fibers: for example, X-ray diffraction method has the shortcoming that the measurement must be restricted to a very limited region of the crystal in the sheet. The ultrasonic method is difficult to obtain accurate data because of ambiguity arising from contact between the piezoelectric element and the surface of sheet. Because of data scattering in mechanical and Young's modulus methods, the measurements must be repeated many times. The polarized fluorescence method needs a long time for sample preparation.

Furthermore, the measurements of the complex dielectric constant at microwave frequencies are also useful for studying

the relaxation due to the local motion of polymers in sheet materials. Only a few reports^{15, 44} have been presented on dielectric properties of polymers at microwave frequencies, although there have been many^{14, 19, 23, 27, 29} at audio frequencies. These reports have been restricted to polymer films with no voids. Actually, it has been very difficult to determine the fiber orientation of sheet materials and the anisotropy of complex dielectric constant at microwave frequencies because of the paucity of instruments available for microwave dielectric measurements. Thus, it has long been desired to find a method and an instrument for accurately determining the fiber orientation from the dielectric anisotropy at microwave frequencies.

For this purpose, the author has found a new method and developed an instrument, which utilizes polarized microwaves and is free from any contact and destruction of sample sheets. The new type of instrument consists of a pair of rectangular waveguides with a narrow gap in which the sample is set. This method allows him to determine the fiber orientation of sheet materials such as paper, nonwoven fabrics, and cow leather and their complex dielectric constant at microwave frequencies.

Chapter 1 of the text describes in detail the principle of determining the fiber orientation by the new method using microwaves, the evaluation of orientation pattern and complex dielectric constant at microwave frequencies, and also the construction of instrument and the method for measurements employed for the present study.

Chapter 2 is concerned with determination of fiber orientation for paper sheets without contact in as short a time as 30 s by the new microwave method. The orientation

patterns determined from the microwave method are compared with the results obtained by the other conventional methods such as mechanical breaking strength and polarized infrared absorption. The present microwave method is made clear to be a very convenient one for determination of fiber orientation.

Chapter 3 is devoted to fiber orientation determined from the anisotropy of complex dielectric constant for paper sheets by using microwaves. The dielectric anisotropy at 4.0 GHz for paper sheets is compared with the result obtained by the mechanical breaking strength. The degree of orientation in the cross machine direction (CD) perpendicular to the machine direction (MD) is studied for paper sheets. Furthermore, the dependence of complex dielectric constant on the density of paper sheets is also described for studying the effects of voids in paper.

Chapter 4 shows the fiber orientation determined from the dielectric anisotropy of nonwoven fabrics and cow leather sheets at microwave frequencies. A variation in basis weight is also determined from that in the resonance frequency obtained for the nonwoven fabrics. The present microwave method gives an important information for determining orientation of polymer fibers in the nonwoven fabrics and collagen fibers in the cow leather, respectively.

Finally, conclusions from the present investigation are summarized.

CHAPTER 1

Principle and Instrumentation for Determination of Dielectric Anisotropy of Sheet Materials by Use of Microwaves

1.1 Introduction

It has been long required to find a new method for accurately determining the fiber orientation and dielectric anisotropy of sheet materials, since the conventional methods need a long time to determine the fiber orientation and have some disadvantages. For such a requirement, the author has found a new method and developed an instrument for the accurate determination by use of microwaves. This chapter describes the principle of determining fiber orientation based on the new method using microwaves and the method for evaluating the orientation pattern and the complex dielectric constant at microwave frequencies. The construction of the instrument and the method for the measurements are also described. The microwave method allows the orientation of fibers to be determined in a short time.

1.2 Principle

For high polymers, there have been observed, in general, a few or more kinds of dielectric relaxation designated α , β , γ , and so on from the high temperature range.^{14, 51} The relaxations α and β (γ) were assigned, respectively, to the micro-Brownian motion of long flexible dipoles and to local motions such as twist or rotation of short dipoles attached to the polymer chains.^{14, 24} The β or γ relaxation for polymers

are usually observed at low temperatures below room temperature.

Only a few fundamental studies^{15, 44} have been reported on dielectric relaxations at microwave frequencies because of a technical problem, though many studies have been made at frequencies below 10 MHz with an aim of investigating the relationship between the motions of molecular chains and their structure in polymer films.^{14, 16, 19, 23, 24, 27-29, 51}

The microwave region (300 MHz - 30GHz) corresponds to that of the frequencies at which the dielectric relaxations ascribable mainly to the local motion should be observed at room temperature.^{14, 16, 23, 24} It is well known that at low temperatures and at audio frequencies the dielectric anisotropy due to local motions reflects the molecular orientation of polymer chains.^{16, 19} Such an anisotropy, which depends on the orientation of molecular or fiber chains in sheet material, may be determined from the angular dependence of interaction between polarized microwaves and the material. The interaction, which can be detected as change in the intensity of the transmitted microwave, depends on the rotation angle of the anisotropic sheet material. The dielectric anisotropy may also allow the author to be determined at microwave frequencies without contact.

1.3 Resonance Curve and Orientation Pattern

The dielectric properties (dielectric constant ϵ' and dielectric loss ϵ'') of the sheet materials at microwave frequencies are determined from a resonance curve in the cavity resonator system. If the frequency of the polarized microwaves irradiated to the sample in the resonator system is

swept, the resonance curve is obtained.

The resonance curve in the cavity resonator system before and after insertion of a sample is expressed in terms of the frequency dependence of the transmitted microwave intensity as

$$I(\theta) = I_{1,0}(\theta) / \{1 + Q_i^2(\theta) [f_{1,0}(\theta)/f - f/f_{1,0}(\theta)]^2\} \quad (1.1)$$

Here, I , $I_{1,0}$, and Q_i ($i=1,2$) are the transmitted microwave intensity at a given frequency f , its value at the resonance frequency $f_{1,0}$ defined by one at a maximum of the transmitted microwave intensity in the resonance curve, and the ratio of the resonance frequency to the half width Δf in the resonance curve, respectively, all at a rotation angle of θ . The subscripts 1 and 2 indicate the values before and after the insertion of sample.

Actually, it can be seen in Fig.1.1 that the insertion of the sample shifts the resonance frequency f_0 to the lower side and also diminishes I at f_0 . The resonance frequency shifts depending on the capacity part of dielectrics, while the change in intensity at the resonance peak depends on that in dielectric loss. Therefore, the anisotropy in the ϵ' and ϵ'' of the sheet materials gives the different resonance curves at different directions in the sheet plane. Figure 1.2 shows the dependence of I in a range from 3982.600 to 3984.050 MHz for the biaxially stretched polyethylene terephthalate (PET) film with a 100 μm thickness in different directions or at different rotation angles θ .³⁷ A curving mountain chain is observed within 360°. The mountain chain is cut at the selected frequency and the orientation pattern is obtained from the angular dependence of I at this frequency. It may be

appropriate to adopt an orientation pattern, i.e., the angular dependence of transmitted microwave intensity obtained by cutting the three-dimensional pattern at a fixed frequency. The fixed frequency should be selected above the resonance frequency, where the transmitted microwave intensity is one-half that at the resonance frequency in the resonance curve which is located at the lowest frequency side. This frequency is most appropriate,³⁷ in that anisotropic data such as the ratio I_{max}/I_{min} of the maximum-to-minimum intensity (MOR) are most sensitive around it. The orientation angle independent of sample thickness coincides with the direction of main

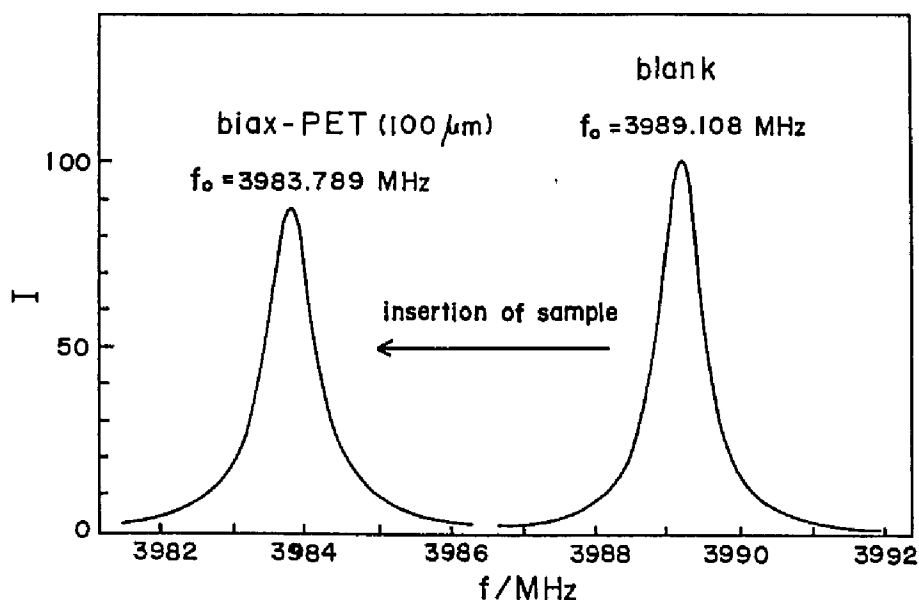


Fig.1.1 Frequency dependence of transmitted microwave intensity I observed at a fixed angle in the resonator system before and after insertion of a biaxially stretched PET film with a thickness of 100 μ m. The resonance frequencies f_0 before and after the insertion of the PET film are 3989.108 and 3983.789 MHz, respectively.

chains of fibers. Since the orientation pattern gives information on the MOR and the orientation angle, it is very convenient for estimating the orientation of molecules or fibers accurately and nondestructively. This pattern also reflects the distribution of fibers. The desired pattern can be also obtained by cutting the three-dimensional pattern at the fixed frequency.

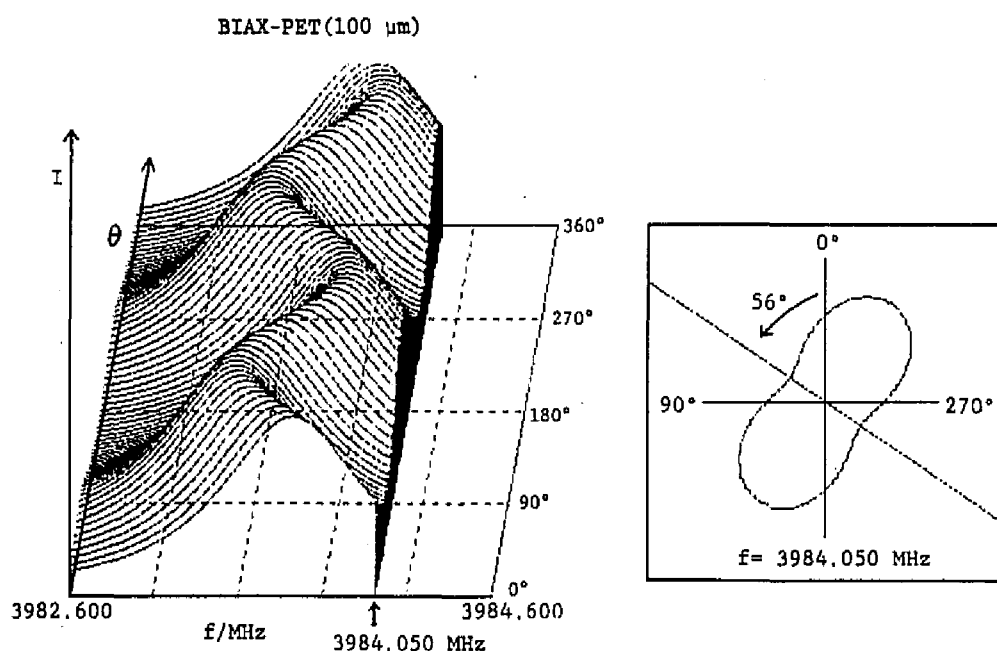


Fig.1.2 Three-dimensional pattern and orientation pattern for the biaxially stretched PET film of 100- μm thickness. The three-dimensional pattern was cut at a frequency of 3984.050 MHz, and the orientation pattern was obtained from the angular dependence of transmitted microwave intensity at the frequency of 3984.050 MHz. The orientation angle was determined to be 56° at which the resonance curve is located in the lowest side.

1.4 Complex Dielectric Constant

A perturbation theory is applicable for the determination of the complex dielectric constant when the sample volume must be very small compared with the cavity itself so that a frequency shift which is small compared with the resonance frequency of the empty cavity is produced by the insertion of the sample. The cavity perturbation method can be used when ϵ'' is very small.¹

The complex dielectric constant $\epsilon^* (= \epsilon' - j\epsilon'')$ for a dielectric sheet is expressed by

$$\epsilon^* = 1 - [(\omega_2 - \omega_1)/\omega_2] [2 \int_{V_s} |F_1|^2 dV / \int_{V_s} |F_1| |F_2| dV] \quad (1.2)$$

where ω is the complex angular frequency, F the electric field in the cavity, V_s the total volume of the cavity, V the volume of the sample, and the subscripts 1 and 2 refer to the values before and after insertion of the sample, respectively. Here, the field F_1 in the cavity is presumed to be known and only the perturbed field F_2 in the sample volume V_s remains as an unknown. The field F_2 is found only in context with a knowledge of sample geometry and of F_1 . The expression relating complex angular frequency to real frequency f and Q -value is derived as

$$(\omega_2 - \omega_1)/\omega_2 = (f_{20} - f_{10})/f_{10} + (j/2)(1/Q_2 - 1/Q_1) \quad (1.3)$$

When the sample is a sheet material and its size is larger than that of the opening of each waveguide, the dielectric constant ϵ' and the dielectric loss ϵ'' are given by

$$\epsilon' = 1 + A(c/t) (f_{10} - f_{20}) / f_{20} \quad (1.4)$$

$$\epsilon'' = (Bc/2t) (1/Q_2 - 1/Q_1) \quad (1.5)$$

or

$$\epsilon'' = (Bc/2t) (1/Q_1) (\sqrt{I_{10}/I_{20}} - 1) \quad (1.6)$$

Here, c is a parameter related to the depth of the rectangular waveguides, t is a thickness of sheet sample, and A and B are constants associated with a narrow gap between a pair of rectangular waveguides in the instrument. Equations (1.4) and (1.5) or (1.6) indicate that ϵ' can be determined from the relative shift in the resonance frequency and ϵ'' from a decrease in the Q value reflecting the sharpness of the resonance curve or a reduction in transmitted microwave intensity at the resonance frequency. Thus a dielectric anisotropic sheet is expected to give different resonance curves in different directions of rotation angles in the sheet plane.

1.5 Construction of Instrument

The microwave cavity resonator system consists of a pair of rectangular waveguides with a narrow free space in which the sheet sample is set. The cavity resonator is shown in Fig.1.3, which details the x , y and z directions, as well as the interior cavity dimensions a , b and c . The waveguides have an oscillator in a side and a detector in the other side, as shown in Fig.1.4. Polarized microwaves irradiated to the sheet are oscillated from the oscillator while the transmitted microwave intensity through the sheet is detected by the detector. The oscillator consisted of cavity type and its

stability in power output and frequency was very good. The detector consisting of a GaAs semiconductor was used. The narrow gap of 5 mm length between a pair of waveguides was made so that the Q-value should not be reduced in comparison with that in the ideal cavity with no gap. It was very important to set the cross sections of both waveguides in parallel and to rotate the sample sheet whose plane is in parallel to the cross sections. The dimensions of the rectangular waveguides denoted by Japanese Standard WRJ-4 were 58 mm for a , 29 mm for b , and 110 mm for c . Here, the dimension of c corresponds to a distance between two irises which correspond to vacant circles with a 9 mm diameter. Each iris was connected with an oscillator and a detector, respectively. The position of the narrow gap in the waveguides was determined to be in the center of the cavity between two irises so that the magnitude of the electric field excited by the oscillator should have a maximum at the sample position. The resonance frequency and Q-value were mainly 4.0 GHz and 6000 in the empty cavity, respectively. The mode of the

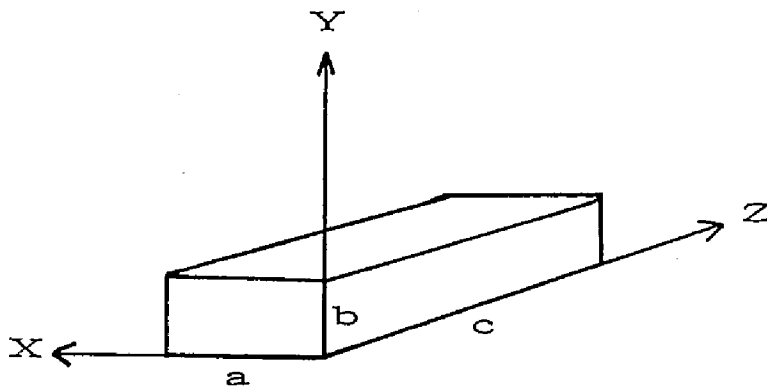


Fig.1.3 Cavity resonator system with interior dimensions a , b and c in the x , y and z directions, respectively.

electromagnetic field was a transverse electric wave (TE) of a type $TE_{1,0,L},^{1,0}$ with L being odd number.

The block diagram of the instrument is shown in Fig.1.5. A sample sheet in the sample holder is placed in the narrow gap in the cavity resonator system. The polarized microwaves were irradiated vertically to the sample sheet, which was rotated for 6.0 s around the central axis normal to the sheet plane. The rotation of the sheet was regulated by a controller. The transmitted microwave intensities were

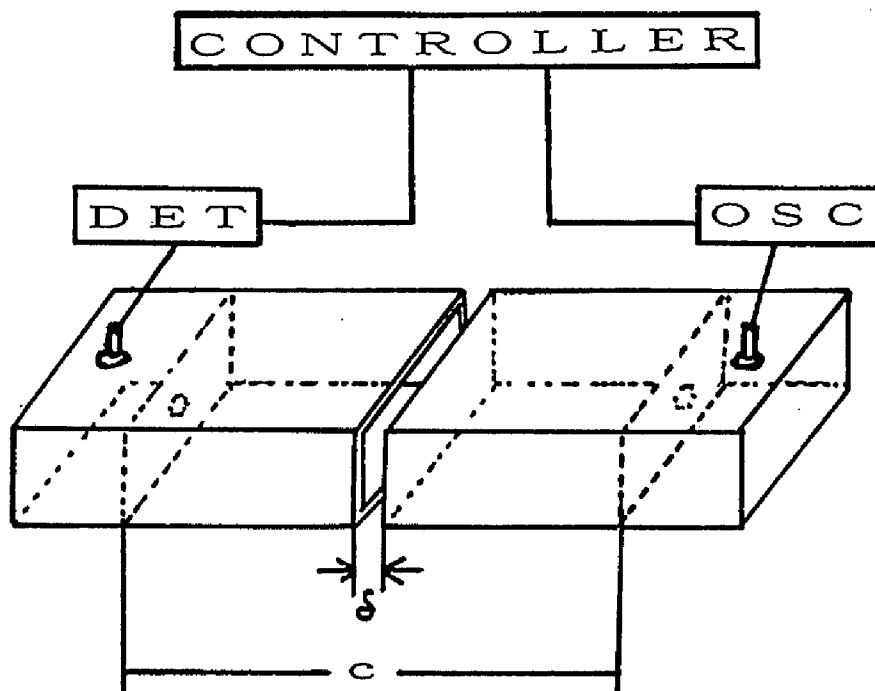


Fig.1.4 Cavity resonator system consisting of a pair of rectangular waveguides with a narrow gap of b . The sample sheet is inserted into the gap, and the cavity resonator is connected with an oscillator and a detector by two irises.

detected by a detector and are digitalized for each rotating angle. The angular dependence of transmitted microwave intensity corresponds to an orientation pattern.

The controller part regulated the rotating angle. A batch of 360 data points were fed into Central Processing Unit (CPU) of a computer. All the results were displaced on a Cathode Ray Tube (CRT) and recorded by the printer, including the orientation pattern, a measuring frequency, an orientation angle between the main axis of molecular or fiber chains and a fixed standard direction, the observed maximum I_{max} and minimum I_{min} intensities, and the ratio MOR of the

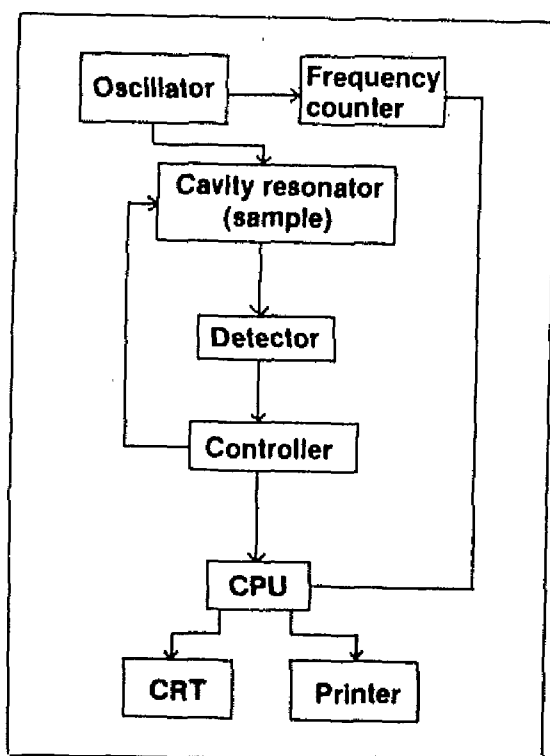


Fig.1.5 Block diagram of the analyzer.

maximum to minimum intensities. The attenuation in microwave intensity can be obtained from the change in intensity of the incident transmitted microwaves. Since the ratio MOR depends on the sample thickness, a comparison between the ratios at a constant thickness is of meaning for samples with different thicknesses. This ratio should be a measure of the orientation distribution of molecular or fiber chains for the sample with almost the same thickness. Further, the ratio CD/MD of intensities in the CD to the MD or the stretching direction calculated were also displayed on the CRT and recorded on a chart. The data processing time was about 2 s.

According to the specification and functions described above, the instrument for the experiments in the present study was developed in 1983 by the author(see Photo.1), and denoted by a microwave molecular orientation analyzer model No. MOA-2001A.

1.6 Method for Measurements

The experimental procedure is as follows: The test sample, cut to a fixed size, is set at a standard direction in the cavity resonator system, the frequency is adjusted above the resonance frequency by a dial as described Section 1.3 , and the measurement is made by putting the computer key board. After rotation of sample for 6.0 s, the orientation pattern is obtained(see Fig.1.2).

The resonance frequency and the half-width in the resonance curve were searched by sweeping frequency with a tuner rotated, and the ϵ' and ϵ'' were determined as described in Section 1.4. Then, the sample was rotated to different angles around the central axis normal to the sheet plane, and

measured successively to determine ϵ' and ϵ'' . It took about 3 min to obtain the complete angular dependence of ϵ' and ϵ'' at every 30°. The measuring frequencies were mainly 3.2 to 4.0 GHz.

All measurements were made at 20 °C and 65% RH. The paper sheets used in the present study usually contained about 6 % water.

1.7 Conclusion

A new method and a new type of instrument was developed for accurately determining the fiber orientation from the dielectric anisotropy by use of microwaves. The instrument consists of a pair of rectangular waveguides with a narrow gap in which the sample sheet is set. The polarized microwaves are irradiated vertically to the sheet, which is rotated for 6.0 s around the central axis normal to the sheet plane. The instrument makes him determine the fiber orientation from the orientation pattern and the dielectric anisotropy by use of microwaves.

CHAPTER 2

Fiber Orientation Pattern of Paper Sheets

2.1 Introduction

The fiber orientation in paper sheets has been studied by mechanical breaking strength,^{11, 30} elastic modulus,⁸ laser light,^{42, 43} ultrasonic velocity⁴⁸ and X-ray diffraction.⁴¹ However, these methods require a long time to determine the orientation and have some shortage of accuracy for measurements. The mechanical breaking strength and elastic modulus measurements do not always give reproducible data because of the destruction of sample. It is also uncertain whether these mechanical methods accurately reflect the orientation in a small portion of the sample sheet, because of the necessity of cutting a number of specimens in different directions. The X-ray diffraction method has the shortcoming that the measurement must be restricted to a small portion of the sheet. The ultrasonic method, which is useful for measuring elastic modulus, suffers from the problem that the data obtained depend on the degree of contact between the piezoelectric element and the sheet. Since the Poisson ratio cannot be determined exactly, it is also difficult to determine the elastic modulus along the machine direction by this method.

Conventional methods are not useful for quality control of products with respect to orientation. Thus, the author has devised such an analyzer, capable of determining the fiber orientation in as short a time as 30 s by utilizing polarized microwaves (see Chapter 1).

For an anisotropic sheet, the resonance curve changes with the direction, in that the transmitted microwave intensity measured at a fixed frequency above the resonance frequency changes at different directions when the sheet is rotated. The dielectric anisotropy caused by local motions reflects the molecular orientation of polymer chains¹⁶ in the amorphous and/or crystalline region. To determine such a molecular or fiber orientation at room temperature, it is necessary to use polarized microwaves. The molecular or fiber orientation in an anisotropic sheet can be determined from the angular dependence of the transmitted microwave intensity, which reflects the dielectric anisotropy at microwave frequencies. Thus, the fiber orientation in an anisotropic paper sheet can be determined by the microwave method.^{31,33}

2.2 Experimental

The experimental procedure for determination of fiber orientation pattern is described in Chapter 1. The samples used in this study were machine-made paper, condenser paper and handsheets with a size of 100 x 100 mm. The polarized FT-IR (Fourier transformation infrared rays) measurements were carried out by means of an analyzer manufactured by Japan Spectroscopic Co., Ltd. The mechanical breaking strength was measured for a machine-made paper and a handsheet with a sample size of 15 mm x 100 mm at a rate of extension of 10 mm/min.

2.3 Fiber Orientation by Conventional Methods

Mechanical Breaking Strength

Figure 2.1A shows the angular dependence of mechanical

breaking strength for a machine-made paper with a basis weight of 38 g/m^2 . Here, the data points show the average values of the breaking strengths measured three times in the same direction. The breaking strength is larger in the MD than in the CD.

Figure 2.1B shows similar results (average of 4 measurements) for a handsheet with a basis weight of 62 g/m^2 . The data show considerable scatter. The angular dependence of breaking strength is seen to be relatively weak, which suggests a nearly random orientation of molecules.

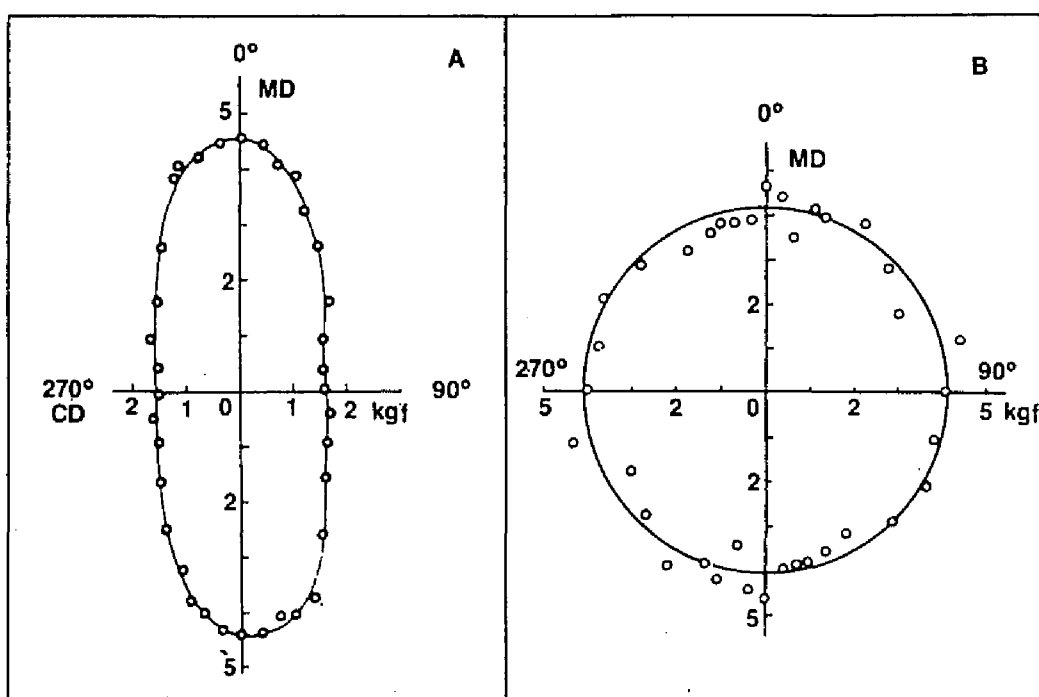


Fig.2.1 Angular dependence of breaking strength in kgf for (A) a machine-made paper with a basis weight of 38 g/m^2 and (B) a handsheet with a basis weight of 62 g/m^2 . The data are expressed in terms of the polar coordinates.

Orientation, by FT-IR Spectra

Polarized FT-IR measurements were carried out for a condenser paper with a thickness of 22 μm . It was necessary to use such a thin and transparent paper so that the irradiated infrared rays should be transmitted through the paper. The polarization of the spectra indicated an anisotropy in the orientation. The angular dependence of absorption at crystalline bands of 1420 cm^{-1} (CH_2 scissoring

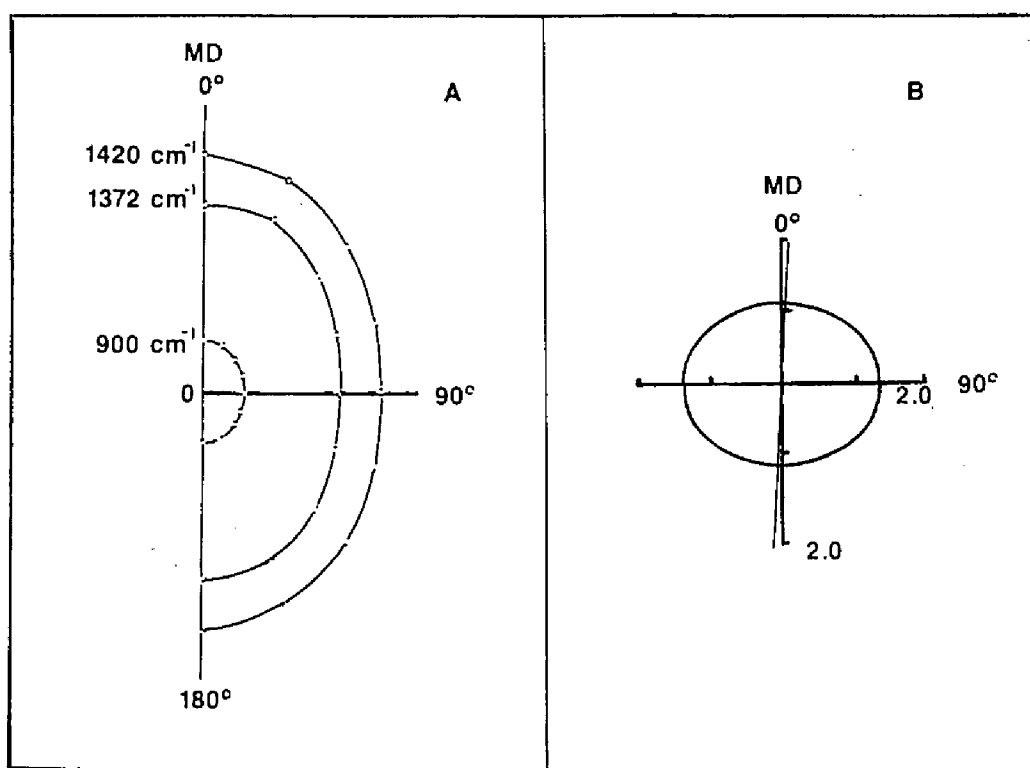


Fig.2.2 A: angular dependence of infrared absorption at crystalline bands of 1420 cm^{-1} , 1372 cm^{-1} , and an amorphous band of 900 cm^{-1} . B: angular dependence of transmitted microwave intensity for the condenser paper (frequency = 3.457 GHz, max = 1.241, min = 1.01, incline = -3° , max/min = 1.229, CD/MD = 1.22). The data are expressed in terms of the polar coordinates.

motion) and 1372 cm^{-1} (CH bending mode), and an amorphous band of 900 cm^{-1} for cellulose²¹ is shown in Fig.2.2A. The sample sheet was placed in a fixed direction by rotation around the normal to the sheet plane, and the polarizer was fixed to the vertical direction.

The results support the idea that the molecular chains in the crystalline and amorphous regions align in the MD. For comparison, the angular dependence of transmitted microwave intensity for the condenser paper is also shown in Fig.2.2B. This pattern shows that the fibers orient in the MD, reflecting the dielectric anisotropy caused by local motions of cellulose chains in the amorphous or crystalline region. Consequently, the orientation values obtained by the microwave method are confirmed by the molecular orientation values obtained by the IR method.

The dichroism of the IR absorption at the band of 1650 cm^{-1} (H_2O deformation vibration) was examined. No appreciable anisotropy of the absorption was observed, suggesting that the water molecules do not align. Hence, the anisotropy shown by the microwave method reflects the fiber orientation, which leads to the orientation of molecular chains of cellulose in the paper sheet.

2.4 Orientation Pattern by Use of Microwaves

Fiber Orientation Pattern

Figure 2.3A shows the angular dependence of microwave attenuation for a machine-made paper with a basis weight of 38 g/m^2 . The microwave attenuation is larger in the MD than in the CD.

As mentioned, it was difficult to decide from the

mechanical breaking strength test of handsheets whether the fiber orientation is truly random or not, because of the data scatter (Fig.2.1B). To measure angular dependence of microwave intensity, a 240 x 190 mm handsheet with a basis weight of 62 g/m² was prepared with a square sheet machine and cut into two samples. The results are shown in Figs.2.3B and 2.3C. Although the dependence is weak in comparison with that for machine-made paper, it is not negligible, i.e., anisotropy is

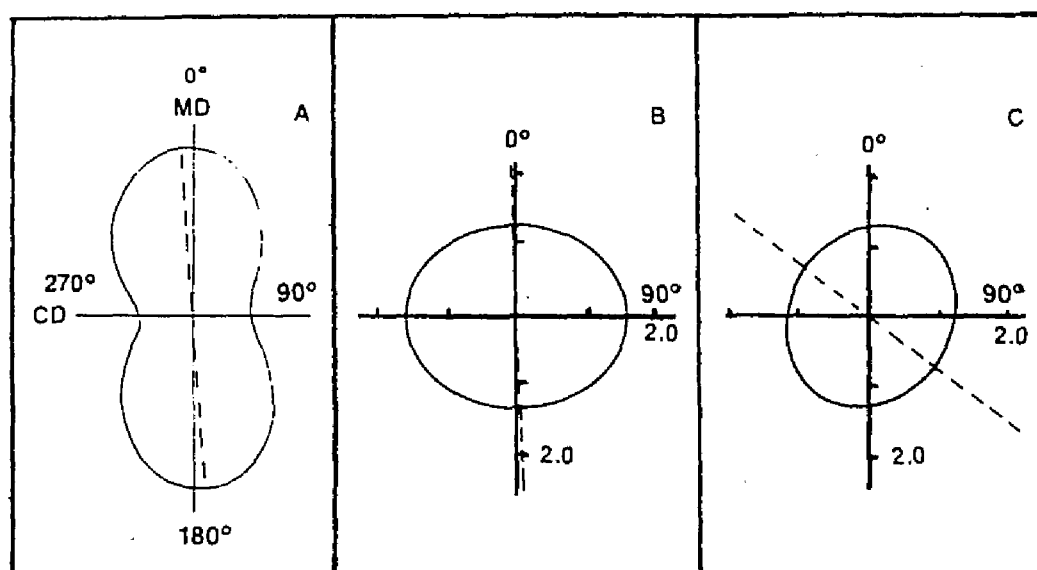


Fig.2.3 A: angular dependence of attenuation in microwaves for a machine-made paper with a basis weight of 38 g/m². B: angular dependence of transmitted microwave intensity at one position for a handsheet with a basis weight of 62 g/m² (frequency = 3.454 GHz, max = 1.344, min = 1.031, incline = 2°, max/min = 1.304, CD/MD = 1.283). C: angular dependence of transmitted microwave intensity at the other position for a handsheet with a basis weight of 62 g/m² (frequency = 3.454 GHz, max = 1.083, min = 0.922, incline = 54°, max/min = 1.175, CD/MD = 0.947). The data are expressed in terms of the polar coordinates.

observed even for a handsheet:

Fiber Orientation Angle

The orientation angles determined from the microwave method did not change with water content for a machine-made paper and showed a nearly constant value, indicating that the orientation angle is essentially independent of water content (see Fig.2.4). However, it was very difficult to accurately determine the orientation angle for the paper sheets with water content above 15 % which gave an almost circular pattern.

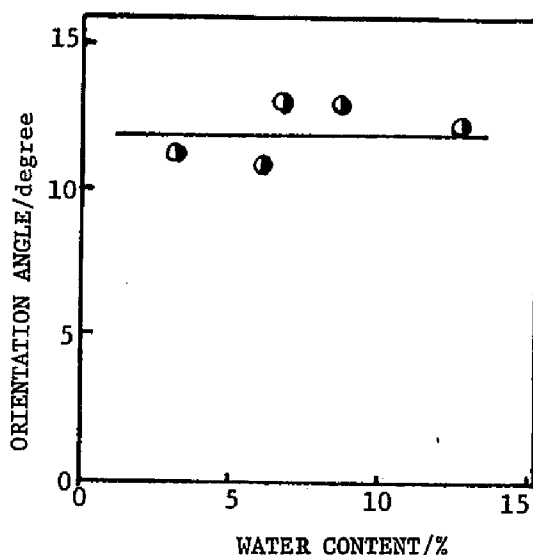


Fig.2.4 Dependence of water content upon orientation angle for a machine-made paper with a basis weight of 71 g/m². The orientation angle was determined by the microwave method.

The chemical composition of the water affects the orientation patterns. For example, the chemical composition with high values of dielectric constant and loss at microwave frequencies reduced the transmitted microwave intensity but did not change the orientation angle.

It is useful to compare the orientation angle determined from the microwave attenuation with that determined from the angular dependence of the mechanical breaking strength in order to examine whether the orientation angle by the microwave method is reliable. The relationship between the orientation angles determined from mechanical breaking strength and from the microwave attenuation was studied for a machine-made paper with a basis weight of 38 g/m² which gives different orientation angles at different positions of the CD (angle θ to MD). The mechanical orientation angle θ_{me} and the microwave orientation angle θ_{mw} determined at the same position of the CD were found to be related by the expression

$$\theta_{me} = 0.87 \theta_{mw} \quad (2.1)$$

The correlation coefficient between these two orientation angles was 0.92, good correlation. Thus, the microwave method was found to give a reliable orientation angle. However, since the principles of the two methods are different, θ_{me} and θ_{mw} does not necessarily agree with each other.

Ratio of Transmitted Microwave Intensity, MD to CD

The relationship between the ratios Y of maximum to minimum of breaking strength and those of X of maximum to minimum of transmitted microwave intensity was examined for a

machine-made paper. The ratio Y increased with increasing X:

$$Y \propto CX \quad (2.2)$$

The coefficient C depends only on sample thickness. Therefore, ratio X determined from the microwave method is substantially as a measure of anisotropy determined from the mechanical method.

2.5 Change in Fiber Orientation in Cross Direction

Figure 2.5 shows the orientation angles determined from the angular dependence of microwave attenuation for a machine-made paper with a basis weight of 66 g/m² at a frequency of

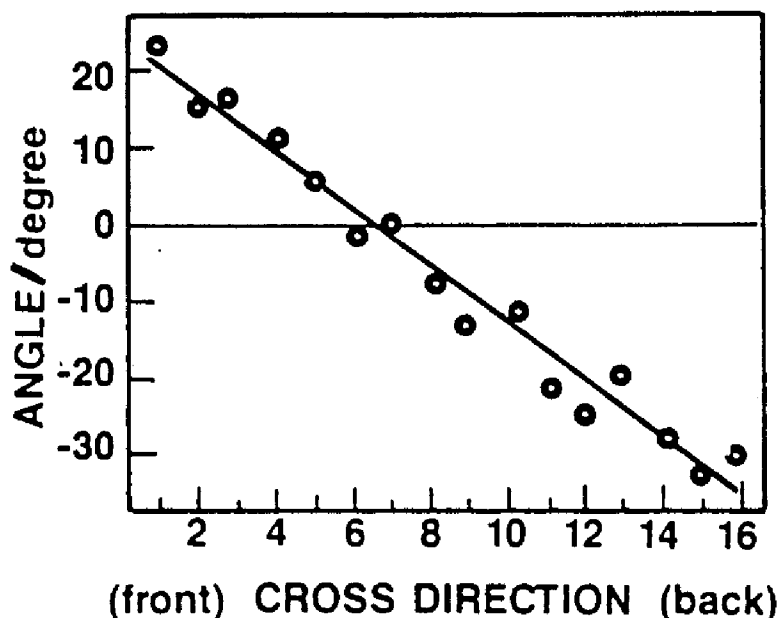


Fig.2.5 Orientation angles for a machine-made paper with a basis weight of 66 g/m² at a frequency of 3491.11 MHz. The samples are numbered from 1 to 16 front to back side along the CD.

3491.110 MHz. Samples in 16 different portions were prepared by cutting a 2200 mm width sheet. The representative orientation patterns are shown in Fig.2.6. Among three different areas (front, center, and back) in the CD of the machine-made paper, the orientation angle is large in the

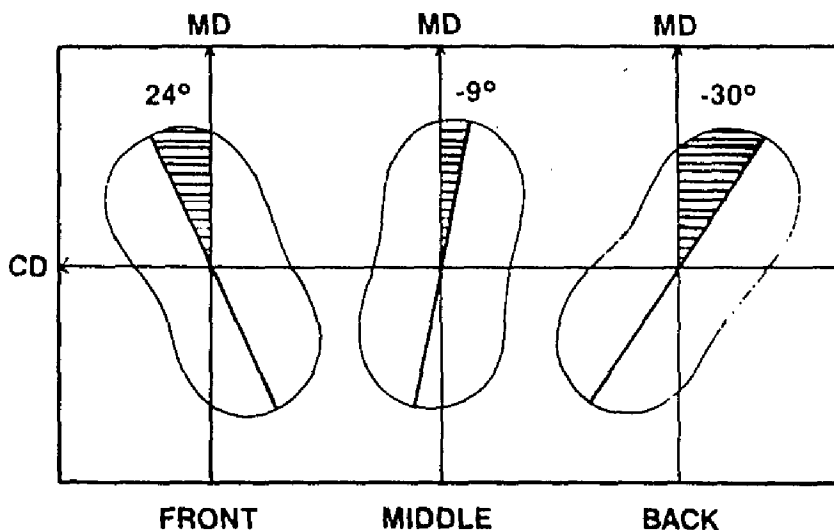


Fig.2.6 Representative orientation patterns in the CD for the machine-made paper.

front and back but small in the center. This finding suggests that the axis of the molecular or fiber chains deviates from the MD for the edges, while the molecular or fiber chains are almost parallel to the MD for the center.

2.6 Conclusions

A new analyzer allows an accurate determination of the fiber orientation for sheet materials such as paper. Better for examining the anisotropy of a paper than the mechanical strength method, the analyzer is useful for both research and

quality control as a method for measuring orientation nondestructively. This microwave method is based on the anisotropy resulting from the local motion of cellulose molecular chains with dipole moments. The method was substantiated by IR and mechanical breaking strength methods.

CHAPTER 3

Relationship between Fiber Orientation and Dielectric Anisotropy in Paper Sheets

3.1 Introduction

Few studies^{16, 28} on dielectric anisotropy at audio frequencies have been reported, because the preparation of different samples such as randomly oriented and uniaxially oriented films requires a long time. Because the fine structure of molecular or fiber chains differs from sample to sample, it is essential to measure the dielectric anisotropy with the same sample. The dielectric measurements with contact at audio frequencies suffer from difficulties arising from incomplete deposition of metal on rough surfaces of paper sheet consisting of pulp fibers and voids. For such paper sheets the dielectric measurements at microwave frequencies, which eliminates the needs for contact between sample and electrodes, would give useful information on the fine structure of fibers in paper sheets.

It is important to study the effect of density on dielectric properties of paper sheet since the paper sheet consists of pulp fibers and voids.^{17, 25, 26} In Chapter 2, the author described the determination of fiber orientation for paper sheets by means of microwaves. Furthermore, it is useful to study the fiber orientation from the complex dielectric constant at microwave frequencies and the density dependence of complex dielectric constant for discussing the physical properties of paper sheets quantitatively.

Present chapter describes an attempt to determine the fiber

orientation from the dielectric anisotropy^{3,4} and then to study the density dependence of dielectric properties of paper sheets by using microwave method.^{3,6}

3.2 Experimental

The samples used were tetrafluoroethylene-hexafluoroethylene copolymer films, handsheets, machine-made paper, uniaxially oriented paper, and condenser paper. The tetrafluoroethylene-hexafluoroethylene copolymer films were previously found to be random in molecular orientation by the microwave method. The handsheets were prepared from hardwood pulps beaten in a Niagara beater. Canadian standard freeness(CSF)^{4,6} for the hardwood pulps ranged from 100 ml to 700 ml. The pulps was fractionated by a classifier of Clark type according to fiber length, and handsheets were prepared from each fraction. The screen meshes of classifier were 14, 24, 42 and 80 wires per inch. The density of handsheet was higher for smaller mesh and lower freeness. Handsheets with different densities were also prepared by changing the pressure of wet pressing for a pulp with a freeness of 580 ml C.S.F. The handsheets prepared from softwood pulps were also used. A uniaxially oriented paper with a basis weight of 41 g/m² and a density of 0.48 g/cm³ was prepared by using an oriented sheet former manufactured by Kumagai Riki Co. The machine-made paper with a basis weight of 60 g/m², a density of 0.81 g/cm³, and a 2800 mm width was also prepared at a machine speed of 650 m/min. The condenser paper with a basis weight of 28 g/m² and a CSF of 200 ml had a high density of 1.43 g/cm³.

The mechanical breaking strength was measured for

uniaxially oriented sheet with a basis weight of 41 g/m² and a size of 15 mm(width) x 100 mm(length) prepared at a stretching rate of 10 mm/min by use of an Instron. The electron microphotographs were obtained using a scanning microscope JSM T300(Japan Electron Optics Laboratory Co.).

The density of each paper was determined by measuring its weight and thickness. The thickness was measured with a micrometer. In the study of density dependence, the average values of ϵ' and ϵ'' at angles of 0° and 90° were used for eliminating the effect of anisotropy of handsheets.

Figure 3.1 shows ϵ' at 4.0 GHz for tetrafluoroethylene-hexafluoroethylene copolymer film with different thicknesses. It can be seen that ϵ' is about 2.04, independent of thickness. A change in ϵ' was less than 1 % even when the electromagnetic mode was changed. For such a film, the value of 2.05 had been reported at 1.0 GHz,⁴⁷ in good agreement with

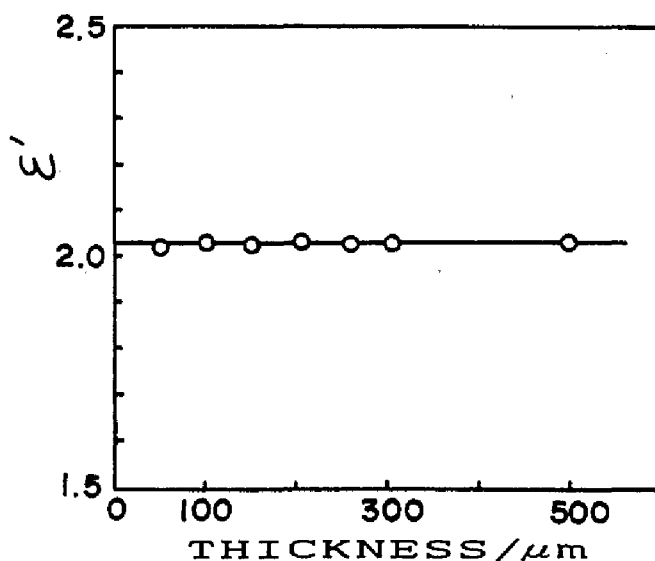


Fig.3.1 Thickness dependence of dielectric constant ϵ' at 4.0 GHz for tetrafluoroethylene-hexafluoroethylene copolymer.

our value obtained by the analyzer. This agreement may be taken as showing the reliability of our method for determining the dielectric constant at a frequency of 4.0 GHz.

The refractive index n for the sheet materials can be derived from the Maxwell equation⁹. When ϵ'' of dielectric material is very small and the magnetic permeability is assumed to be unity the following equation is obtained:

$$n = (\epsilon')^{1/2} \quad (3.1)$$

3.3. Anisotropy of Complex Dielectric Constant

Figure 3.2 shows ϵ' and ϵ'' at 3.4 GHz for a uniaxially oriented paper with a basis weight of 41 g/m² and a density of

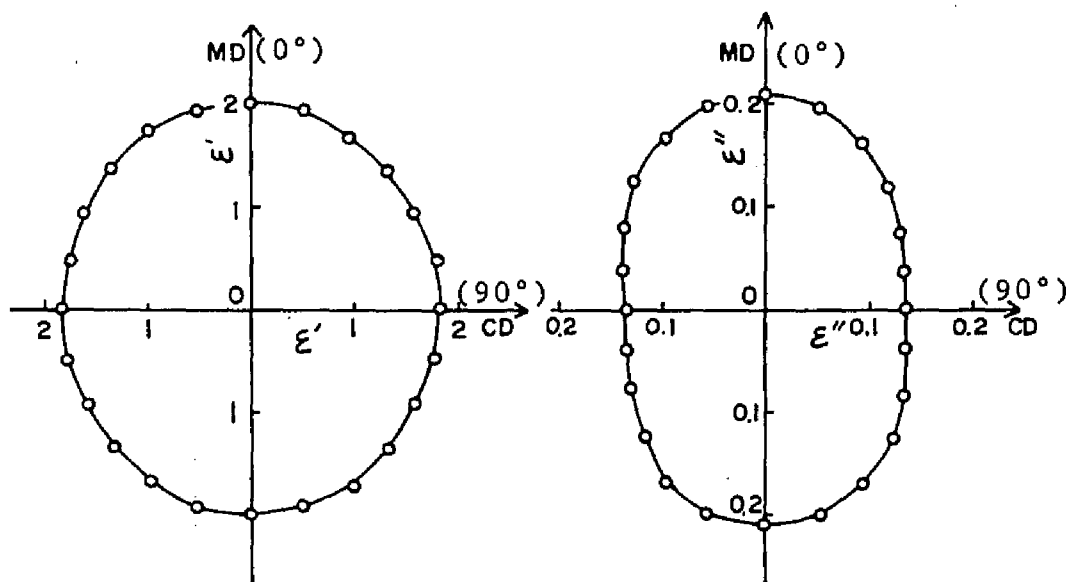


Fig.3.2 Angular dependence of dielectric constant ϵ' and dielectric loss ϵ'' at 3.4 GHz for a uniaxially oriented paper with a basis weight of 41 g/m² and a density of 0.48 g/cm³. The data are expressed in terms of the polar coordinates.

0.48 g/cm³. Both ϵ' and ϵ'' in the MD are larger than those in the CD which is perpendicular to the MD. The ϵ' value of ca. 2.0 suggests that the paper sample should contain many voids in comparison with a condenser paper. In other words, this dielectric constant is an apparent value for the bulk paper constituting pulp fibers and voids. In fact, the density was very low.

The electron microphotograph taken for the surface of the uniaxially oriented paper is shown in Photo.2. It suggests that the pulp fibers orient in a preferable direction on an average. The electron microphotographs for the cross section in the MD and the CD also given in Photo.2 show that most pulp fibers in the MD within the plane of the paper, and support the above suggestion that the paper contains many voids.

Figure 3.3 shows the angular dependence of ϵ'' at 3.4 GHz for a condenser paper with a low CSF of about 200 ml and a high density of 1.43 g/cm³. The density is nearly equal to those of pulp fibers.³ The direction of the maximum ϵ'' corresponds to that of the maximum in polarized infrared absorbance (see Fig.2.2),³⁰ suggesting that the main chains of cellulose molecules orient predominantly in the direction of maximum ϵ'' . The dielectric constant for the condenser 4.2~4.5 (at 3.4 GHz), which indicates that this paper has a condensed texture of pulp fibers.

For comparison, the angular dependence of mechanical breaking strength for the uniaxially oriented paper with a density of 0.48 g/cm³ is shown in Fig.3.4. The breaking strength in the MD is larger than that in the CD, indicating that the pulp fibers orient mainly in the MD, as found above from electron microphotographs.

The relation between the dielectric constant ϵ' and the mechanical breaking strength S for a uniaxially oriented paper was found to be expressed, in a first approximation, by the following empirical equation:

$$S = -24.1 + 13.6 \epsilon' \quad (3.2)$$

with a correlation coefficient between S and ϵ' of 0.93 and a standard deviation of 0.37. In more strict treatment, S may be expressed in terms of a quadratic equation of ϵ' , it was found that

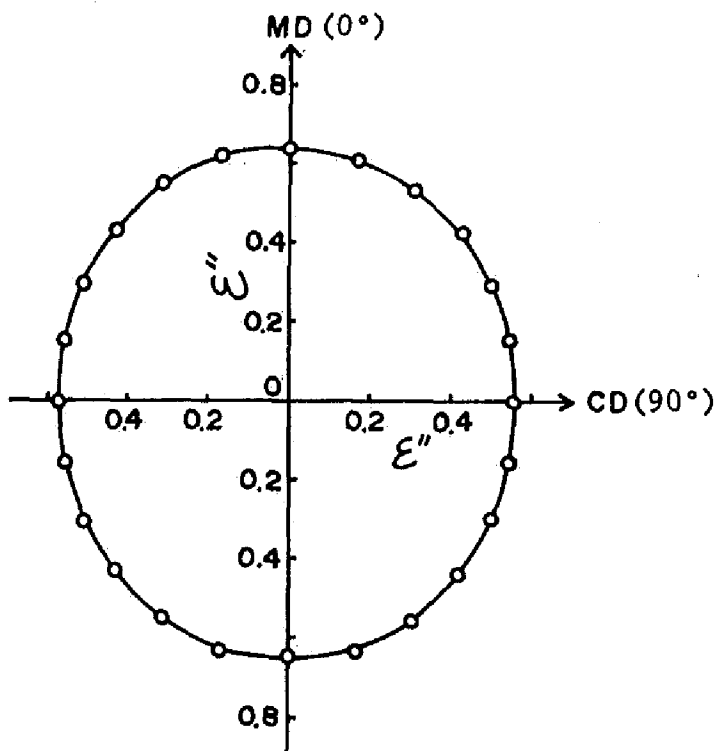


Fig.3.3 Angular dependence of ϵ'' at 3.4 GHz for a condenser paper with a basis weight of 28 g/m² and a density of 1.43 g/cm³. The data are expressed in terms of the polar coordinates.

$$S = 282.1 - 30.4 \epsilon' + 824.0 \epsilon'^2 \quad (3.3)$$

with a standard deviation of 0.31 (see Fig.3.5).

The relationship between S and the dielectric loss ϵ'' for the uniaxially oriented paper could be expressed by

$$S = -3.6 + 32.2 \epsilon'' \quad (3.4)$$

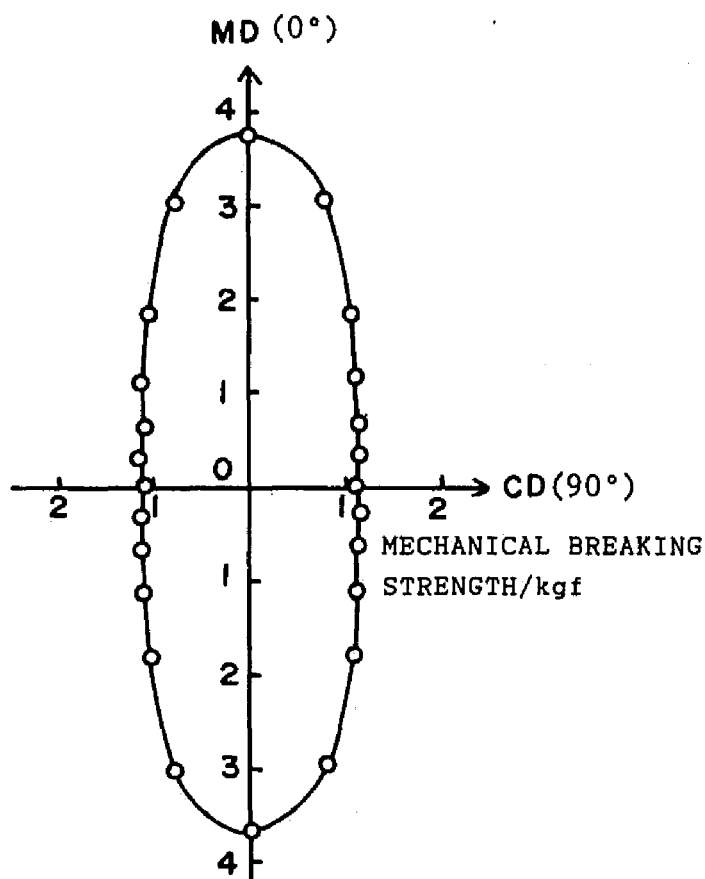


Fig.3.4 Angular dependence of mechanical breaking strength for the uniaxially oriented paper with a thickness of 85 μm , a sample width of 10 mm, a basis weight of 41 g/m^2 , and stretching rate of 5 mm/min. The data are expressed in terms of the polar coordinates.

with a correlation coefficient of 0.92 and a standard deviation of 0.40 or by

$$S = 15.3 - 189.4 \epsilon'' + 536.5 \epsilon''^2 \quad (3.5)$$

with a standard deviation of 0.222 (see Fig.3.5). Thus, we may conclude that good correlation exist between ϵ' and S and between ϵ'' and S.

As discussed above, the dielectric data reflect the anisotropy of the cellulose molecules rather than the macroscopic pulp fibers, while the mechanical anisotropy is considered to originate from the arrangement of the pulp fibers. It is well established by X-ray diffraction^{18, 45} that

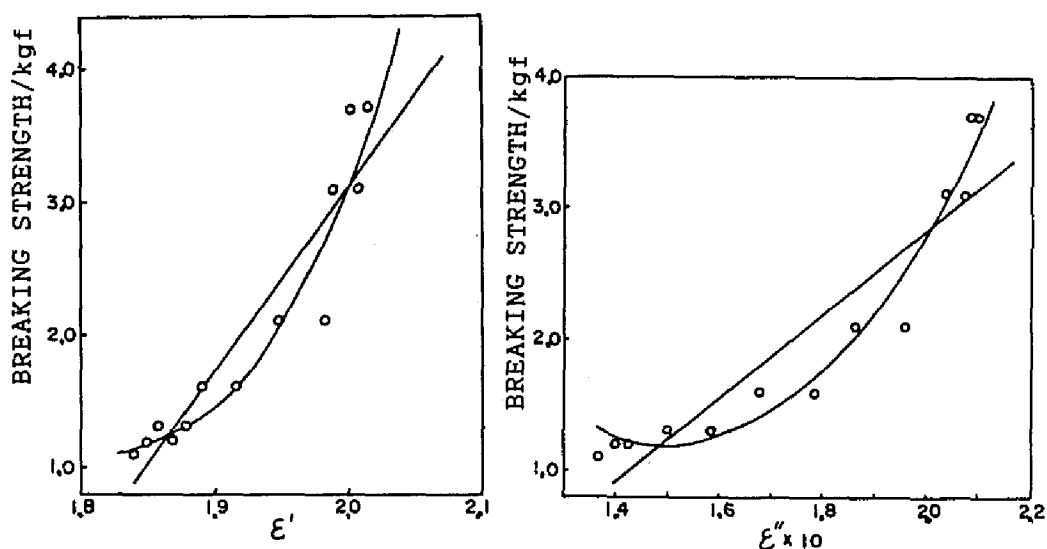


Fig.3.5 Relationships between the mechanical breaking strength S and the dielectric constant ϵ' and between S and the dielectric loss ϵ'' at 3.4 GHz for a uniaxially oriented paper with a basis weight of 41 g/m².

cellulose molecules orient on an average along axis of pulp fibers even though the molecules are aligned in a slightly deviated direction from the main axis of the fibers and that the actual fibers are anisotropic in molecular orientation.

The parallel relationship between the dielectric and mechanical anisotropies may be understood reasonably from such a structural character of the paper sheet. The complex dielectric constant for handsheet was essentially independent of the direction, and consistent with the results for the sheet from the mechanical breaking strength which showed no anisotropic behavior.

Figure 3.6 shows the angular dependence of n at 3.4 GHz for

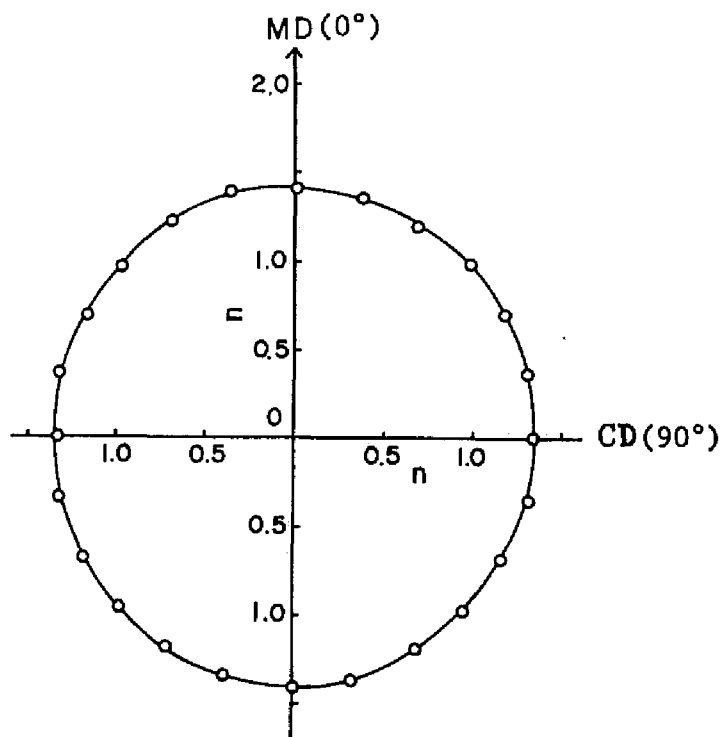


Fig.3.6 Angular dependence of refractive index n at 3.4 GHz for a uniaxially oriented paper with a basis weight of 41 g/m² and a density of 0.48 g/cm³. The data are expressed in terms of the polar coordinates.

the same uniaxially oriented paper as in Fig.3.2. Such an anisotropy can be observed, as is the case for the dielectric constant; from this figure, the birefringence, which can be defined by the difference in n between the MD and the CD, is determined to be 0.075. Since n in different directions can be obtained, birefringences in different directions can also be determined. In this way, the present microwave method allows the refractive index and birefringence even of the opaque materials to be determined.

3.4 Change in Anisotropy in Cross Direction

Figure 3.7 shows the angular dependence of ϵ'' at three different positions (front, center, and back) in the CD for the

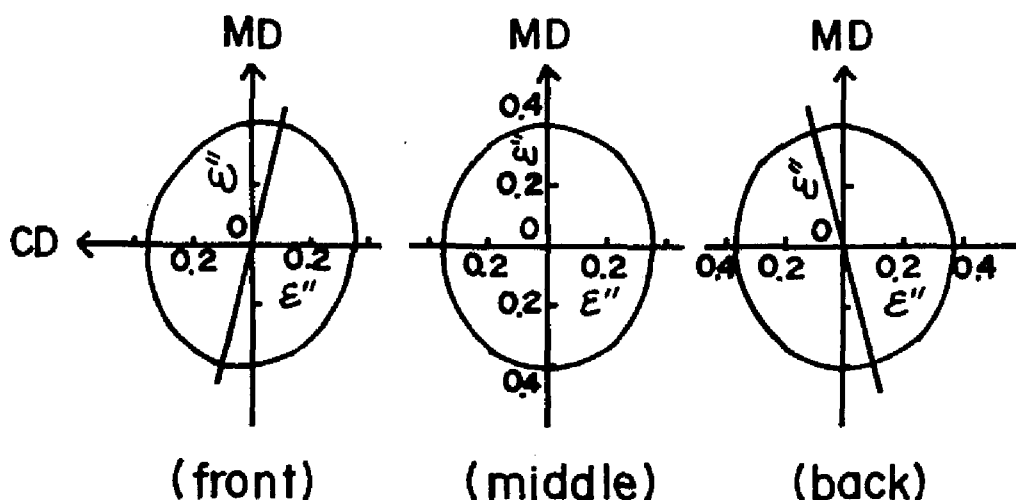


Fig.3.7 Angular dependence of ϵ'' at 4.0 GHz at three different positions (front, center, and back) in the cross machine direction CD for machine-made paper with 2800 mm, a basis weight of 60 g/m², and a density of 0.81 g/cm³.

machine-made paper with a basis weight of 60 g/m², a density of 0.81 g/cm³, and a 2800 mm width; samples were prepared by cutting a 2800 mm wide sheet to 28 different portions. The patterns differ at different positions. The orientation angles defined as the direction of maximum ϵ'' relative to the MD are plotted against the different positions in the CD in Fig.3.8. However, the orientation angle did not change for

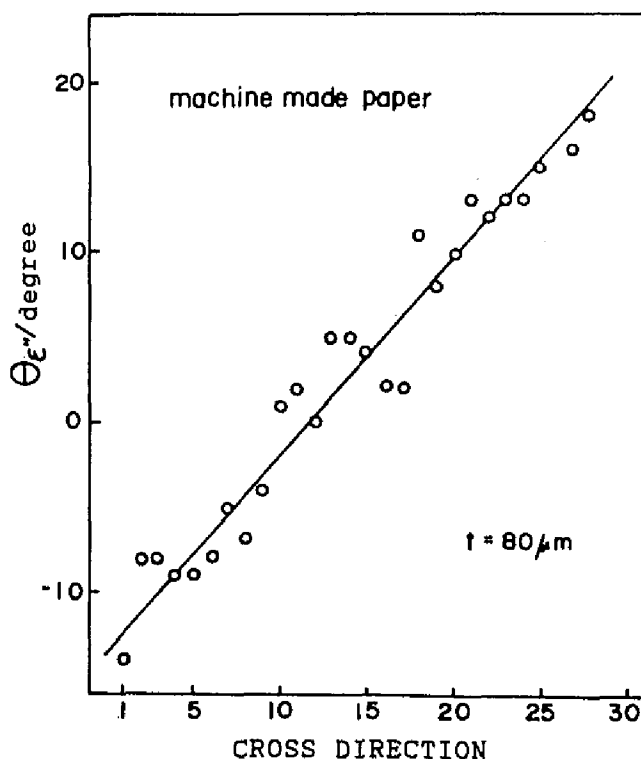


Fig.3.8 Orientation angles determined from the angular dependence of ϵ'' at 4.0 GHz for the samples prepared at 28 different positions in the CD of machine-made paper with a width of 2800 mm, a basis weight of 60 g/m², and a density of 0.81 g/cm³. The samples are numbered from 1 to 28 from left to right side along the CD.

different positions in the MD. Thus, angular dependence of complex dielectric constant reflects the distribution of pulp fibers within the paper plane.

The orientation angle was larger in the front and the back, but smaller in the center. This finding suggests that the axis of molecular chains in the center is oriented mainly in the MD.

In Fig.3.9, the maximum to minimum ratio of ϵ'' is plotted against different positions in the CD for the machine-made paper with a basis weight of 60 g/m² and a density of

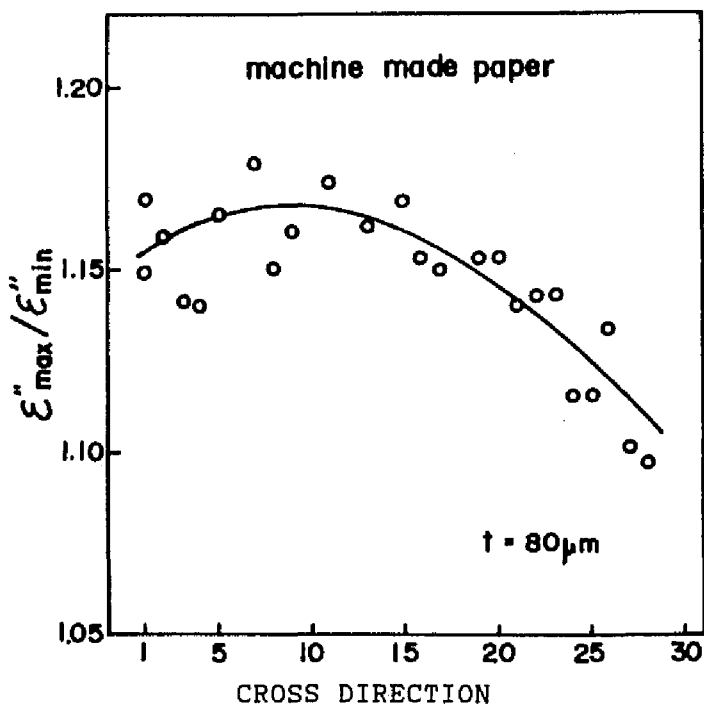


Fig.3.9 Maximum to minimum ratio of ϵ'' at 4.0 GHz at many different positions in the CD of machine-made paper with a width of 2800 mm, a basis weight of 60 g/m², and a density of 0.81 g/cm³. The samples are numbered from 1 to 28 from left to right side along the CD.

0.81 g/cm³. The ratio $\epsilon''_{\max}/\epsilon''_{\min}$, which gives a measure for the degree of orientation of pulp fibers, depends on the position in the CD. The ratio decreased with changing position from the center to the back, indicating that the anisotropy is not uniform in the CD.

Figure 3.10 shows a relationship between the ratios of

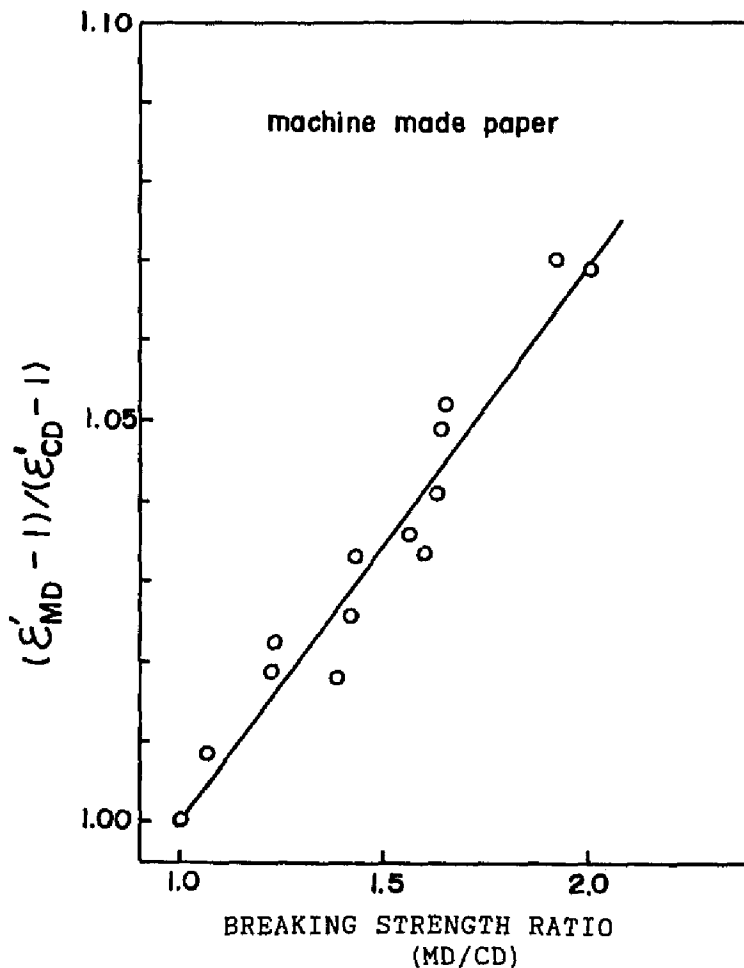


Fig.3.10 Relationship between ratios of $(\epsilon' - 1)$ at 4.0 GHz and of mechanical breaking strength in the MD to CD for machine-made paper with various basis weights.

($\epsilon' - 1$) and of breaking strength in the MD to CD. The dielectric ratio increases almost linearly with increasing mechanical ratio which is a measure of anisotropy. This suggests that the microwave method is useful for estimating the anisotropy without destruction, instead of mechanical breaking strength.

3.5 Density Dependence of Complex Dielectric Constant

Figure 3.11 shows the relationships between ϵ' and ρ and between ϵ'' and ρ at 4.0 GHz, respectively, for various handsheets consisting of hardwood pulps. Both ϵ' and ϵ'' increased linearly with increasing ρ . The indicated straight lines represent

$$\epsilon' = 0.531 + 3.07 \rho \quad (3.6)$$

$$\epsilon'' = -0.098 + 0.619 \rho \quad (3.7)$$

in the range of ρ studied. The correlation coefficient between ϵ' and ρ , and between ϵ'' and ρ were 0.994 and 0.984, respectively.

The relationship between ϵ' and ϵ'' for the handsheets is shown in Fig.3.12. The linear relation can be expressed by

$$\epsilon'' = -0.2144 + 0.205 \epsilon' \quad (3.8)$$

Effect of Freeness

The density of handsheet increased gradually with a decrease in freeness. This increase in density was large

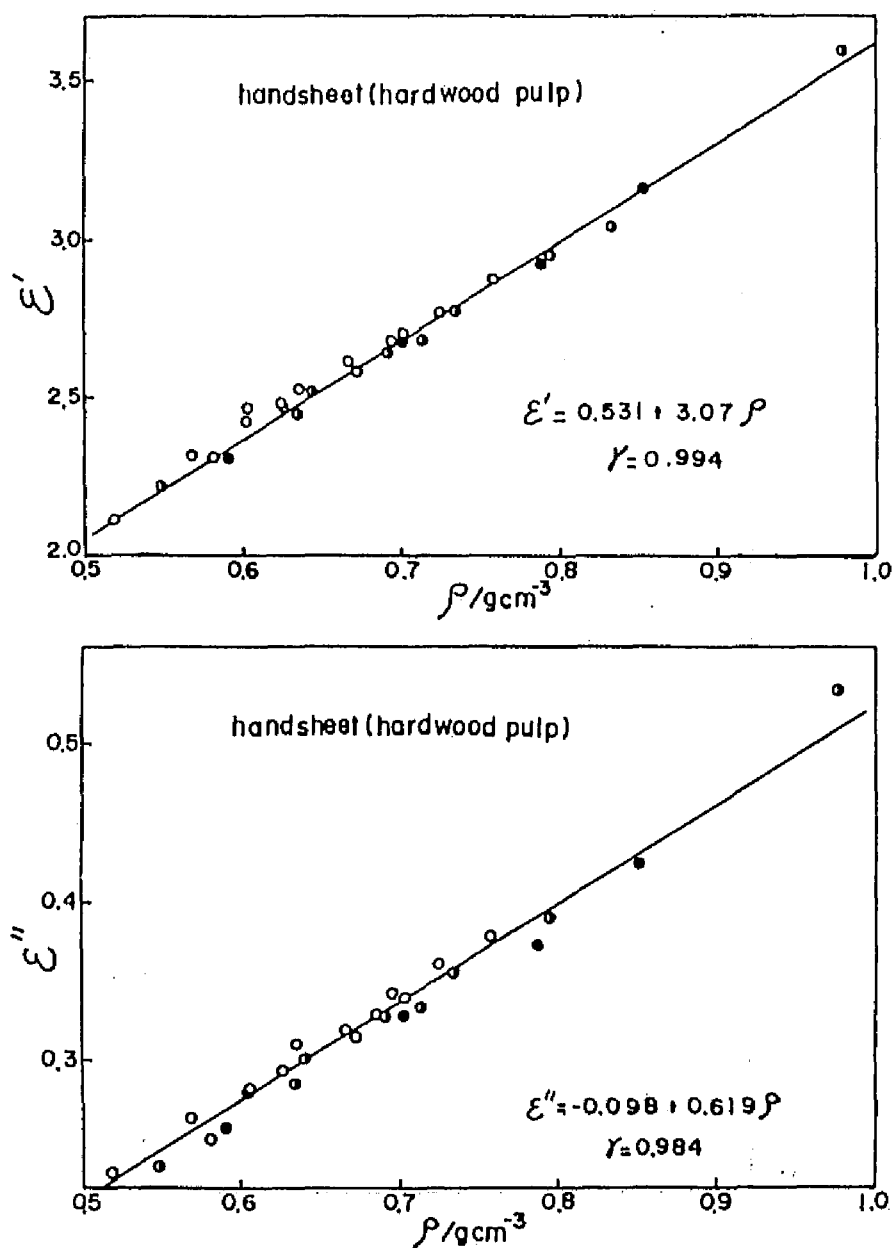


Fig.3.11 Density dependence of ϵ' and ϵ'' at 4.0 GHz for handsheets consisting of hardwood pulps. Handsheets were prepared by three different methods: \odot , beating; \bullet , fractionation; \circ , pressure of wet pressing.

especially at freeness below 200 ml. A lower freeness obtained by beating pulp fibers may be ascribed to more pronounced packing induced by cutting and fibrillation of pulp fibers. The value of ϵ' for handsheets increased especially below a freeness of 200 ml.

Figure 3.11 includes data for handsheets consisting of hardwood pulps with different freenesses of 100 ml to 700 ml.

Figure 3.13 shows ϵ' at 4.0 GHz for mixtures of two kinds of pulps with freenesses of 100 ml and 600 ml C.S.F. It can be seen that ϵ' decreases almost linearly with increasing the

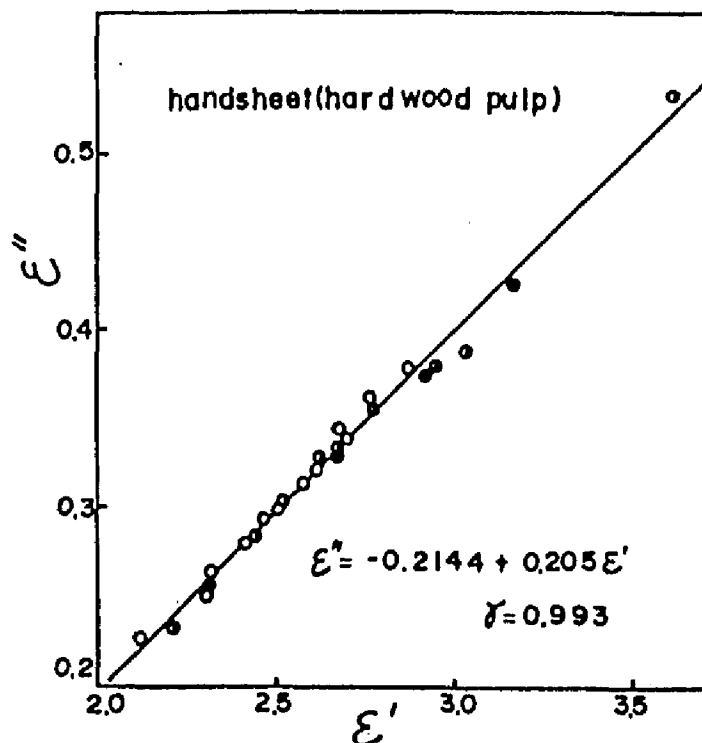


Fig.3.12 ϵ'' at 4.0 GHz plotted against ϵ' for handsheets with different densities. Handsheets were prepared by three different methods: \odot , beating; \bullet , fractionation; \circ , pressure of wet pressing.

content of the pulp of freeness of 600 ml. The decrease in ϵ' may be caused by the decrease in density due to an decrease in the content of pulp with lower freeness.

Effect of Fiber Length

The density of handsheets increased with increasing mesh number (wire per inch). The length of pulp fibers decreased with increasing mesh number. Thus, an increase in mesh number should result in the increase in packing of pulp fibers, leading to an increase in density and have the increase in ϵ' .

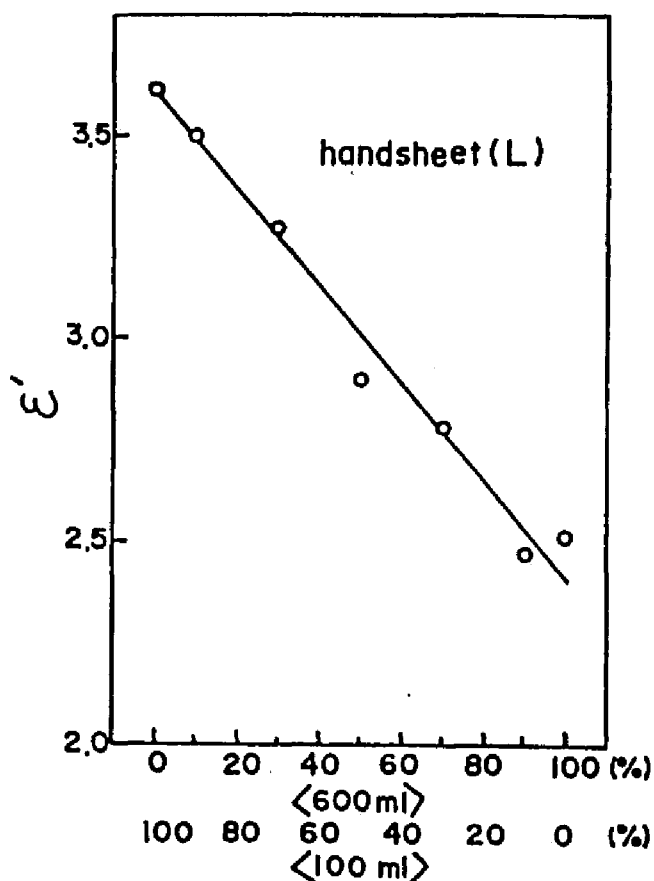


Fig.3.13 Composition dependence of ϵ' for mixtures of two kinds of pulps with freeness of 100 ml and 600 ml C.S.F.

Figure 3.14 shows the density dependence of ϵ' at 4.0 GHz for the handsheets prepared by fractionated pulp fibers with screens of 14, 24, 42, and 80 mesh. As expected, ϵ' increased with increasing mesh number; note that density dependence of ϵ' for the handsheets fractionated with different meshes has been shown in Fig.3.11.

Effect of Pressure under Wet Press

Figure 3.11 also includes data for the handsheets prepared by wet pressing with different pressures. The density of the handsheets increased with increasing pressure. This is

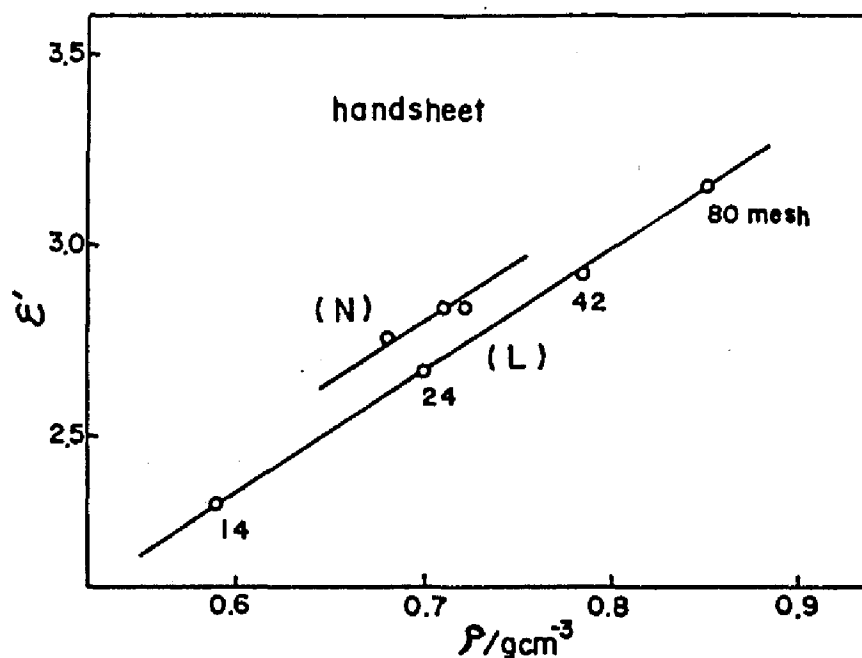


Fig.3.14 Density dependence of ϵ' at 4.0 GHz for handsheets consisting of hardwood pulps (L). The figures of 14, 24, 42 and 80 are the mesh numbers. The handsheets consisting of softwood pulps (N) are used only for comparison with hardwood pulps (L).

related to the increase in ϵ' and ϵ'' with increasing density observed in the figure.

3.6 Discussion

Dielectric Anisotropy

In this study, it was found that only apparent values of ϵ' and ϵ'' were obtained for the machine-made paper sheet containing many voids. These values should approach the values intrinsic to pulp fibers when the content of voids is increased. An increase in voids increases with paper thickness t . Thus, according to eqs. (1.4) and (1.5), ϵ' and ϵ'' increases as the density of paper increases. This is because the number of dipoles per unit volume increases. The anisotropy of ϵ' or ϵ'' depends not only on the degree of the average orientation of pulp fibers but also on the density. If ϵ' changes by wet pressing, the change should be due entirely to that of t . However, if the fiber orientation does not appreciably change within the plane of the sheet on wet pressing, i.e., with an increase in density, the molecular anisotropy should be invariant. Our point is that although ϵ' and ϵ'' increase on wet pressing, the ratios of $\epsilon''_{max}/\epsilon''_{min}$ and $(\epsilon'_{max}-1)/(\epsilon'_{min}-1)$ are not significantly affected by the content of voids and are a measure of the dielectric anisotropy of the paper sheet. The effects of voids and thickness are eliminated in these ratios, as described in eqs. (A-5) and (A-6) of APPENDIX.

We obtained $\epsilon''_{max}/\epsilon''_{min} = 1.0$ for a randomly oriented paper and $\epsilon''_{max}/\epsilon''_{min} = 1.49$ for a uniaxially oriented paper. The difference between these ratios may be used for estimating the degree of molecular or fiber orientation. Because of the good

correlations are obtained among the complex dielectric constant, mechanical anisotropy, and electron microscopic observations, we expect that the average orientation of molecular or fiber chains can be inferred from our anisotropic dielectric data.

The remarkable anisotropy of ϵ' and ϵ'' in the polyethylene terephthalate film^{8,2} containing no voids suggests that the dielectric anisotropy is ascribed not to the voids but to the orientation of macromolecular chains. The angular dependence of ϵ'' for the condenser paper in Fig.3.3 shows the same thing.

Since the angular dependence of polarized infrared absorbance and mechanical breaking strength also shows a maximum in the MD, the cellulose molecules must be oriented on an average in the MD where the long axis of pulp fibers orients mainly. Hence, the dielectric anisotropy may be explained as the result of local motions which leads to a change in dipole moment in the direction of main axis of cellulose molecules.

An effect of water on dielectric behavior was observed. For example, ϵ' and ϵ'' increased with increasing the content of water. However, for the paper containing 5~7% water, ϵ' did not increase appreciably. Therefore, water contributes to the increase in ϵ' and ϵ'' , but does not significantly change the anisotropy of pulp fibers. However, the orientation of water adsorbed on cellulose molecules could not be observed by FT-IR measurements.^{8,0} Therefore, the changes in ϵ' and ϵ'' because of the presence of water should contribute to a circular pattern in the angular dependence of ϵ' and ϵ'' . In short, although the observed ϵ' and ϵ'' are the superposition of contributions from water and the pulp fibers, the

anisotropy of ϵ' and ϵ'' comes not from the water but from the pulp fibers.

The accumulation of data for ϵ' , ϵ'' , n , orientation angle, and the maximum to minimum ratio of $(\epsilon' - 1)$ and ϵ'' will provide an important data base for manufacturing paper corresponding to needs. Actually these dielectric data are important for studying effects of additives, water content, compactness of pulp fibers, species of pulp in paper, etc., and also for producing the high quality paper with respect to the dimensional stability, such as thermal shrinkage described in Chapter 2.

Drying conditions for paper sheets are undoubtedly important factors affecting fiber orientation. In this work, however, we did not go into this problem; we just focused on developing a quick determination of the complex dielectric constant and the anisotropy of paper sheets by our instrument.

Density Dependence of ϵ' and ϵ''

The density dependence of ϵ' and that of ϵ'' for our handsheets are expressed by empirical formulae (3.6) and (3.7). The dependence can be interpreted by eqs. (A-8) and (A-9) in APPENDIX for the relationship between the density and the number of dipoles per unit volume. We note that formulae (3.6), (3.7) and (3.8) hold for ρ between 0.5 and 1.0 g/cm³ but not for lower densities. The increase in ϵ' caused by increase in density must result from an increase in the number of dipoles per unit volume.⁷ In this work, the density was increased by decreasing freeness, increasing mesh number, and increasing pressure. The difference in the coefficients

between ϵ' and ρ , and between ϵ'' and ρ suggests a possibility that the peak of the dielectric β -relaxation is much deviated from the frequency of 4 GHz. At the present stage, however, it is difficult to interpret the difference strictly because of the complexity in the effect of voids and water upon ϵ' and ϵ'' for paper sheets.

At a given ρ , ϵ' is higher for handsheets with softwood pulps than for those with hardwood pulps, as is shown in Fig.3.14. This fact may be ascribed to difference in the magnitude of the effective dipole moment or the number of dipoles per unit volume between these pulps.

It is known that ϵ' and ϵ'' at 4.0 GHz for handsheets may be ascribed to the local motion of cellulose molecules including adsorbed water molecules in the amorphous region. In order to uniformize the effect of water upon ϵ' and ϵ'' for handsheets and to focus on the influence of sheet density, we preconditioned the handsheets at 25 °C and 65% RH for 10 days.

If the ϵ'' comes from polarization due to reorientation of molecules in the amorphous region, the crystallinity will affect the value of ϵ'' . It is unnecessary to consider the effect of crystallinity upon ϵ' and ϵ'' for the handsheets prepared by wet pressing with different pressure, because the handsheets consist of hardwood pulps with the same freeness of 580 ml C.S.F. On the other hand, it may be necessary to consider the effect of crystallinity upon ϵ' and ϵ'' for the handsheets prepared from the pulps with different freenesses and different mesh numbers because of difference in the crystallinity due to beating of pulps. Actually, however, all data obtained from the samples with different freenesses and different mesh numbers approximately followed the same

empirical formula to that for the samples prepared by wet pressing with different pressures. From this fact, the effect of crystallinity may be negligible for the samples used in the present study. In the future, it is expected to obtain the generalized formulae in a wide range of density by strictly examining the effect of factors such as crystallinity, water content and species of pulp fibers upon ϵ' and ϵ'' for the handsheets.

The characteristics of a paper sheet can be evaluated from the formulae (3.6) and (3.7) if ρ is measured. From the complex dielectric constant estimated from ρ , we can obtain information on the species of pulp fibers, additives and impurities in the unknown paper sheets and then compare them with the standard sample. Such data will also reveal the difference in papermaking method.

3.7 Conclusion

The new type of method using microwaves determines the dielectric anisotropy and refractive index for optically opaque paper sheets. The angular dependence of ϵ' and ϵ'' gives the degree of molecular or fiber orientation, the distribution of cellulose molecules in paper sheets. The density dependence of ϵ' and ϵ'' also gives an important information on the packing of pulp fibers in paper sheet, difference in species of pulps, and the structure and physicochemical properties. The accumulation of data for ϵ' , ϵ'' and n at microwave frequencies gives an important chart for manufacturing the functional paper corresponding to needs.

CHAPTER 4

Fiber Orientation of Nonwoven Fabrics and Cow Leather

4.1 Introduction ,

The present chapter deals with fiber orientation of the sheet materials such as nonwoven fabrics and cow leather which differ from the paper sheets in the fiber structure such as the bonding between fibers.

Nonwoven fabrics consisting of polymer fibers have been used for various purposes such as nappy and breakwater, and the range of their industrial use is expanding rapidly. Thus, the mechanical properties of nonwoven fabric sheets are important from a practical point of view. For example, the mechanical nonuniformity in the plane of the fabric sheets gives such troubles as low tear strength in some directions. Low tear strength is related to the orientational distribution of fibers in the sheets, and the experimental determination of the fiber distribution in the plane of fabric sheet is therefore of basic importance.

Generally, it is time consuming to measure the anisotropy of a nonwoven fabric sheet by the mechanical breaking strength method, which also destroys the sheet. Since any sheet contains a number of voids, the reproducibility of data for the mechanical breaking strength is not good, but there has been no alternative method.

On the other hand, determination of the orientation of fibrous components in a biological tissue is basic to the study of the relationship between the fiber structure and

physical properties of the tissue.^{10, 12, 20} The mechanical breaking strength, X-ray diffraction and electron microscope methods³⁴ have been used for investigating the orientation of fibers. The first method needs a number of specimens prepared from a wide portion of the test sample, while the others have the shortcoming that the measurements must be restricted to a small portion of the tissue. All of them are not always convenient for practical use because a long time is necessary for determining the fiber orientation.

In Chapters 2 and 3, the author showed that a microwave method is useful for accurately determining the fiber orientation of paper sheets. In this work, it was applied to determine the fiber orientation from the dielectric anisotropy of nonwoven fabrics³⁵ and cow leather.³⁸

4.2 Experimental

The samples were nonwoven fabrics consisting of rayon fibers with a basis weight of 43 g/m² and those consisting of polyester fibers with a basis weight of 100 g/m², all prepared by the dry process method. Binders were used for bonding these fabrics. The cow leather sheets were also used with a basis weight of ca. 850 g/m² and a thickness of ca. 1.15 mm. Eighteen specimens with a size of 100 x 100 mm as shown in Fig.4.1 were prepared from a cow leather sheet with a size of 300 x 600 mm and subjected to measurements.

Mechanical breaking strength was measured for a nonwoven fabric with a size of 15 mm(width) x 50 mm(length) at a stretching rate of 50 mm/min and for a cow leather with a size of 5 mm(width) x 50 mm(length) at a stretching rate of 10 mm/min by use of a testing machine manufactured by INTESCO.

Co., Ltd., Japan. Young's modulus was obtained from the slope of a stress-strain curve at low strains. The sample thickness was measured with a micrometer.

Evaluation of Basis Weight

A perturbation theory is also applicable to determination of the complex dielectric constant of nonwoven fabrics. For a sample inserted into a cavity resonator, the resonance frequency f_2 is given by

$$f_2 = f_1 \{1 - [(t' - 1)/cAt]\} \quad (4.1)$$

where c is a parameter related to the depth of the cavity, t is a thickness of the sample, A is a constant associated with the instrument, and $(t' - 1)$ is the dielectric increment at the resonance frequency.

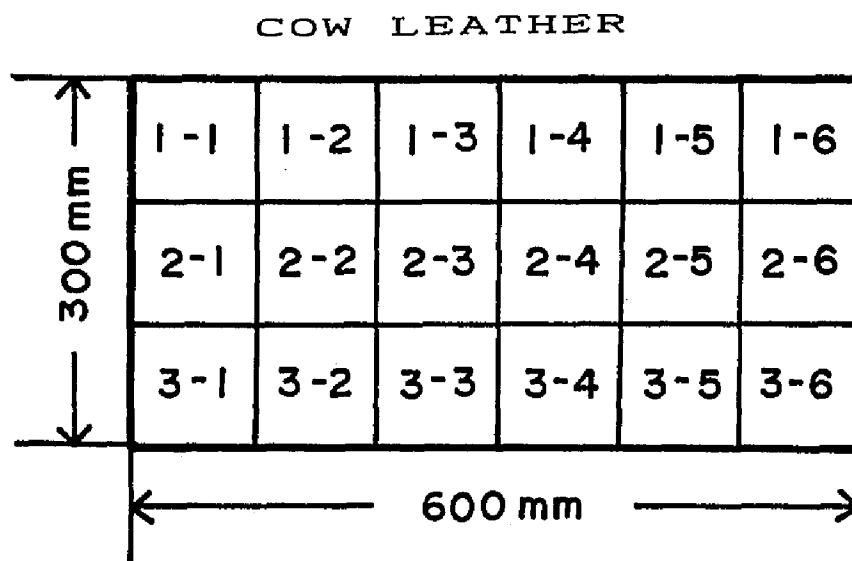


Fig.4.1 Eighteen specimens prepared from cow leather with a size of 300 x 600 mm for the microwave measurements.

When the dielectric relaxation belongs to the Debye type the dielectric increment ($\epsilon'(\omega) - \epsilon'_\infty$) at an angular frequency of ω is expressed by ⁵

$$\epsilon'(\omega) - \epsilon'_\infty = (4\pi N\mu^2/3\epsilon)[1/(1+(\omega\tau)^2)](F_r/F) \quad (4.2)$$

where N is the number of dipoles per unit volume, μ is the dipole moment, ϵ is the restoring force, τ is the relaxation time, F_r is the local electric field, F is the applied electric field, $\epsilon'(\omega)$ is the dielectric constant at angular frequency of ω , and ϵ' is the dielectric constant at high frequencies. Since the density of the sample sheet is defined by the weight per unit volume, it is proportional to N . Putting the dielectric increment in eq.(4.1) equal to that in eq.(4.2), at the angular frequency considered, we have

$$f_2 = f_1 (1 - B\rho t) \quad (4.3)$$

where B is a constant, ρ is a density.

Equation 4.3 is rewritten as

$$f_2 = f_1 (1 - BW) \quad (4.4)$$

where W is basis weight, or weight per unit area.

Thus, we find that f_2 is proportional to W after the sample is inserted.

4.3 Fiber Orientation in Nonwoven Fabrics

Figure 4.2 shows the angular dependence of transmitted microwave intensity at a fixed frequency of 4.0 GHz for

nonwoven fabrics consisting of rayon fibers with a basis weight of 43 g/m^2 . The transmitted microwave intensity is the smallest in the MD. This means that the interaction between the electric field and the fibers in the fabrics is the strongest in the MD.

The orientation pattern is similar to that observed previously for uniaxially oriented paper sheets consisting of pulp fibers. The MOR value of 1.764 determined from the microwave method indicates an anisotropic orientation of fibers in the nonwoven fabrics. The CD/MD value is 1.763. Since the orientation angle is set equal to zero in this case, the orientation pattern suggests that the fibers in the nonwoven fabrics are oriented mainly in the MD. When the fibers are oriented mainly randomly, the transmitted microwave

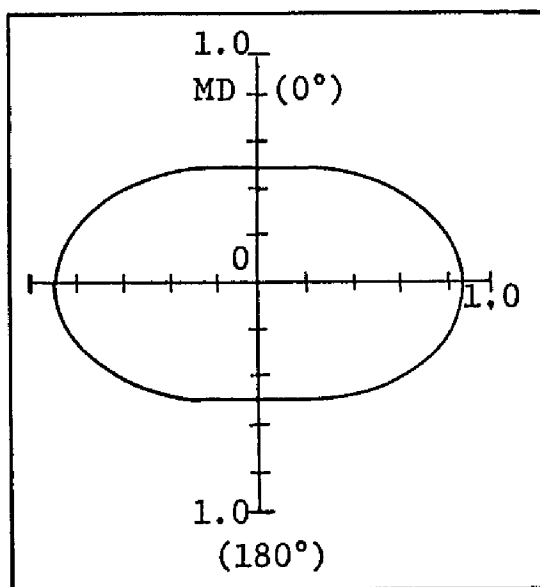


Fig.4.2 Angular dependence of transmitted microwave intensity at a fixed frequency (frequency = 3.98160 MHz, orientation angle = 0° , MOR = 1.764, CD/MD = 1.763, basis weight = 43 g/m^2) for nonwoven fabrics consisting of rayon fibers.

intensities must be almost equal in all directions.

Figure 4.3 shows the angular dependence of ϵ' and ϵ'' at 4.0 GHz for the same nonwoven fabrics as that in Fig.4.2. Both ϵ' and ϵ'' are larger in the MD than in the CD. The angular dependence of ϵ' and ϵ'' is similar to that observed for uniaxially oriented paper consisting of pulp fibers. The unsymmetrical pattern for ϵ'' implies a remarkable anisotropy of the fibers, suggesting that the fibers are oriented mainly in the MD. We found that the angular dependence of ϵ' and ϵ'' gave almost circular patterns for a sample with randomly oriented fibers.

The angular dependence of mechanical breaking strength and that of elastic modulus E for the nonwoven fabric are shown in

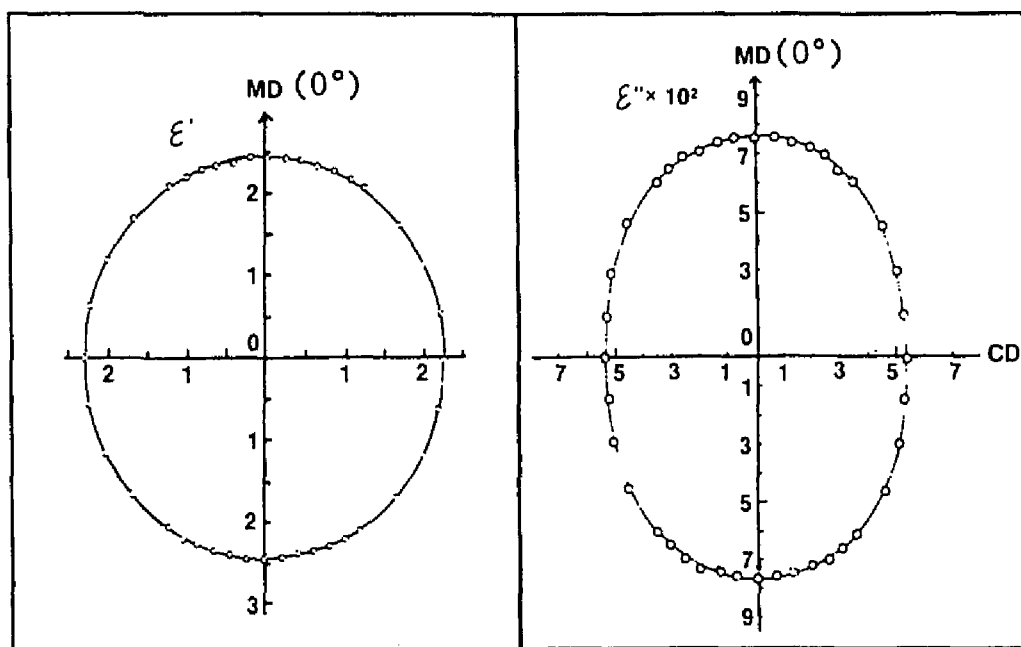


Fig.4.3 Angular dependence of ϵ' and ϵ'' at 4.0 GHz for nonwoven fabrics with a basis weight of 43 g/m². The data are expressed in terms of the polar coordinates.

Fig.4.4. (The sample size was of 15 mm wide x 50 mm long, and the stretching speed was 50 mm/min). Both mechanical breaking strength and the elastic modulus are largest in the MD and smallest in the CD, being consistent with the angular dependence of transmitted microwave intensity and that of ϵ'' .

The electron microphotograph for the surface of the nonwoven fabrics, Photo.3, confirms the suggestion that the

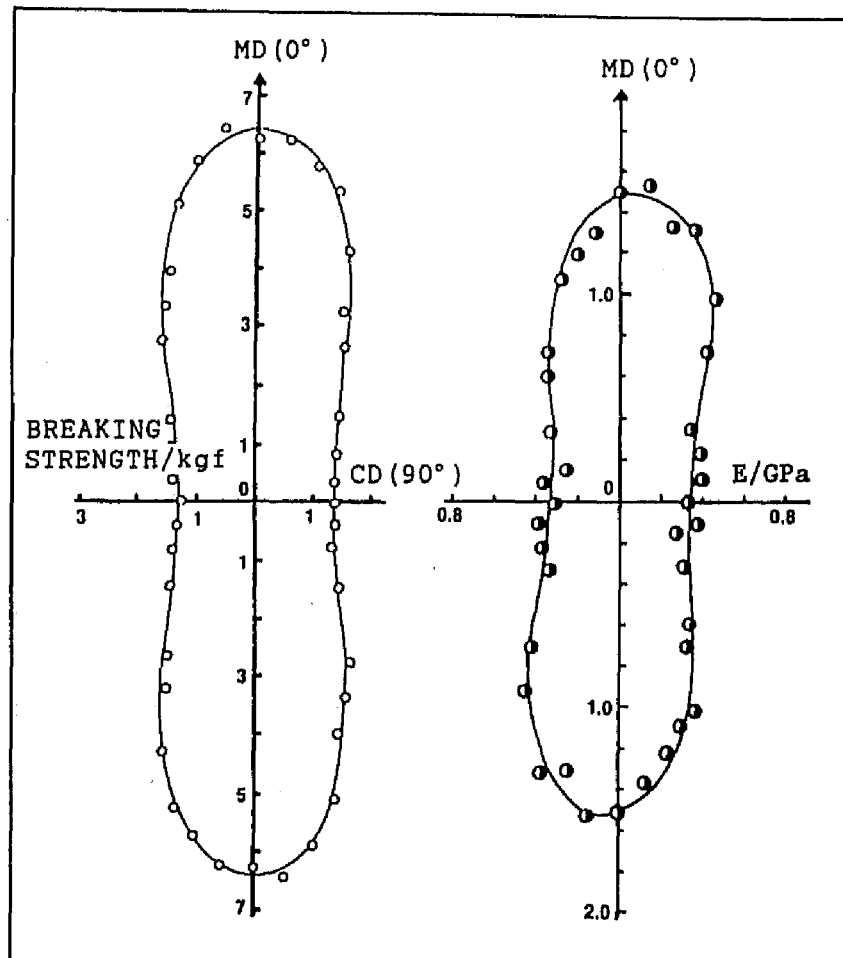


Fig.4.4 Angular dependence of mechanical breaking strength and elastic modulus E for nonwoven fabrics with a basis weight of 43 g/m². The data are expressed in terms of the polar coordinates.

rayon fibers in the nonwoven fabrics are oriented predominantly in the MD. As in Fig.4.4, the direction in the maximum for ϵ' in the MD coincides with that for the maximum in mechanical breaking strength and with that in which the main axes of the rayon fibers are oriented. Such coincidence was also found for uniaxially oriented paper sheets consisting of pulp fibers and voids. Therefore, the author concludes that the fibers of the nonwoven fabrics are oriented mainly in the direction of the maximum in ϵ'' .

Basis Weight

Figure 4.5 shows the dependence of resonance frequency

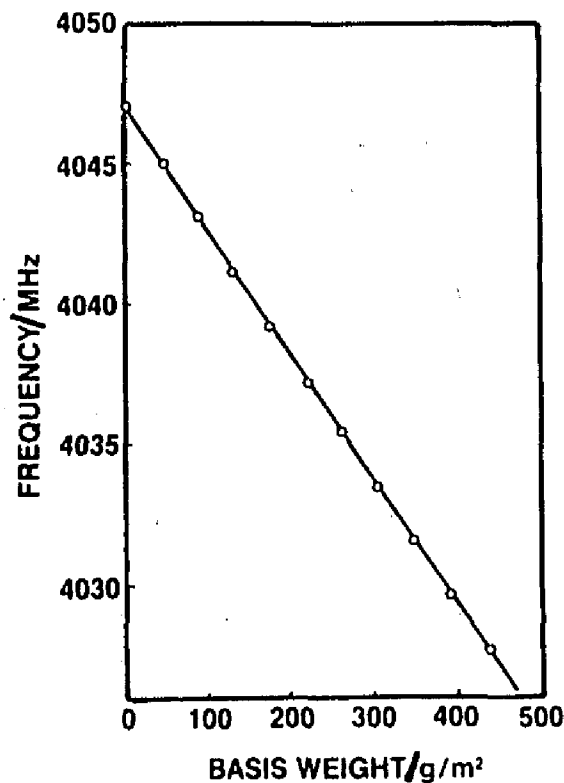


Fig.4.5 Dependence of resonance frequency measurements on basis weight for the nonwoven fabrics with a basis weight of 43 g/m^2 .

measurements on basis weight for the same nonwoven fabrics. Here, the sheets with different basis weights were prepared by piling the fabrics cut successively in the MD. The resonance frequency measured in the MD decreases with increasing basis weight. This decrease can be experimentally expressed as

$$f = 4046.882 - 0.0391 W \quad (4.5)$$

The correlation coefficient between f and W was -0.998 . Here, the numerical constant and coefficient in eq.(4.4) depend on the cavity resonator system and the species of sample, respectively. Since the accuracy in frequency is at most 0.005 MHz, a change of 0.1 g/m² in W should be detected. Thus, f may be used for estimating W . In other words, a variation in basis weight in the CD of sheets may be examined by measuring the resonance frequency.

4.4 Change in Fiber Orientation in Cross Direction

Figure 4.6 shows molecular orientation ratio MOR and orientation angles observed at different positions in the CD for a nonwoven fabrics consisting of polyester fibers with a basis weight of 100 g/m² and a width of 1000 mm. The positions are numbered from one end to the other along the CD of the fabrics. Both molecular orientation ratio and the orientation angle θ change with various positions. The molecular orientation ratio has a maximum near the center in the CD, while θ has a maximum at one end. Figure 4.7 shows

the values of f obtained for the same nonwoven fabrics in the CD. The variation in f reflects the variation in basis weight, which implies that W of the nonwoven fabrics changes with changing position in the CD. The results reveal that the distribution of fibers in the polyester fabrics is not uniform in the CD.

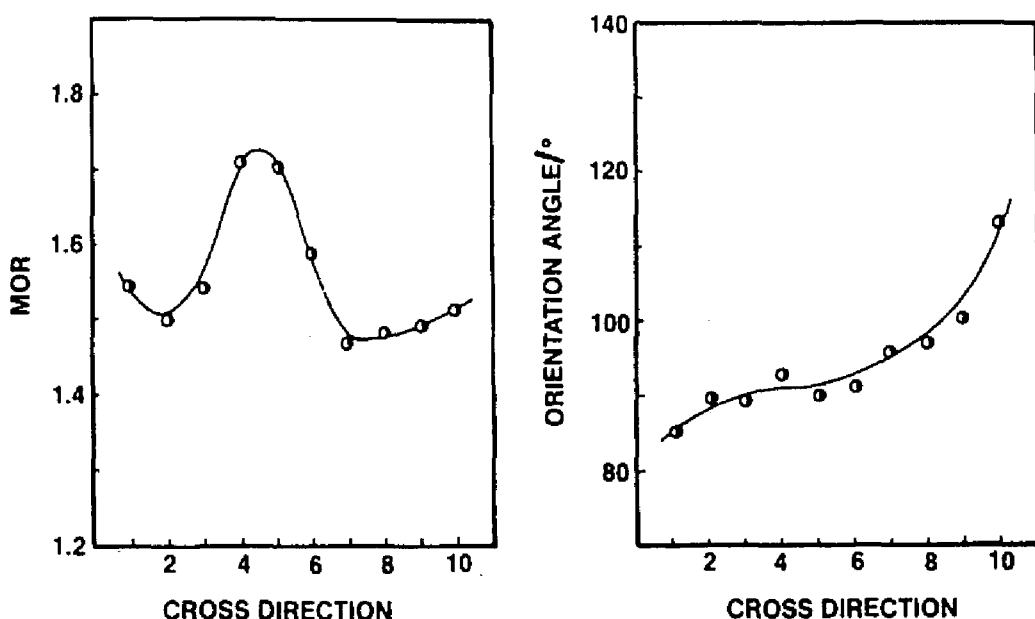


Fig.4.6 Molecular orientation ratio MOR and orientation angle observed at different positions in the CD for a nonwoven fabrics consisting of polyester fibers with a basis weight of 100 g/m^2 and a width of 1000 mm. Molecular orientation ratio is a measure of anisotropy, and orientation angle reflects the main chain direction of fibers (100 g/m^2). The samples are numbered from 1 to 10 from left to right side along the CD.

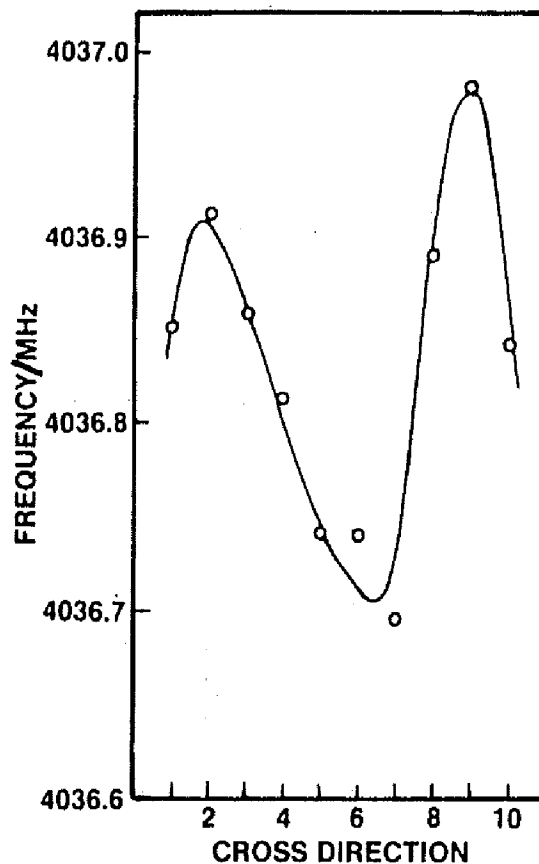


Fig.4.7 Resonance frequency reflects a variation in the basis weight of the nonwoven fabrics (100 g/m^2). The samples are numbered from 1 to 10 from left to right side along the CD.

4.5 Fiber Orientation in Cow Leather

Figure 4.8 shows the angular dependence of transmitted microwave intensity for a cow leather with 1.17 mm thickness and a basis weight of 860 g/m^2 . The angular dependence gives an orientation pattern like an egg cocoon, reflecting a preferable orientation of fibers in the sheet plane.⁵² The direction of the minimum transmitted microwaves, which corresponds to the direction of the maximum attenuation in

microwaves, deviates by 81 degrees from the standard direction SD. The orientation angle and the MOR are determined to be 81 degrees and 2.524, respectively.

Photograph 4 shows an electron micrograph of a cross section of the cow leather sheet. In this photograph, many bundles of fibers with ca. 10 μm or smaller diameters are observed. The fibers are oriented mainly in the direction perpendicular to the surfaces of the sheet plane. The direction of the maximum attenuation in microwaves may correspond to that of the main chains of collagen fibers constituting the cow leather.

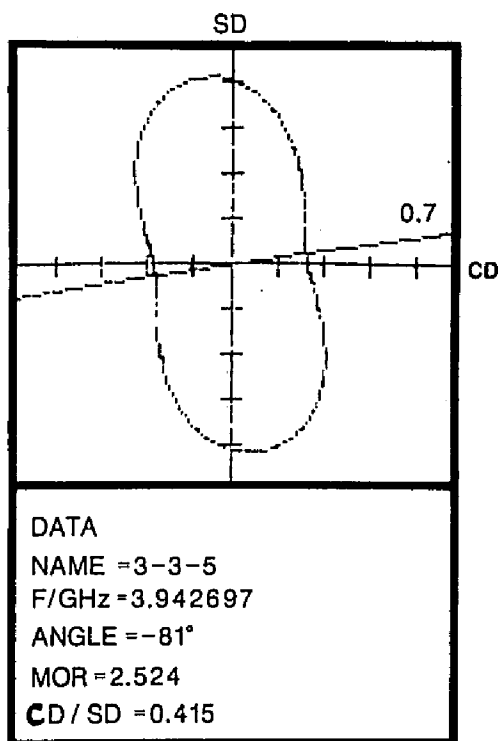


Fig.4.8 Angular dependence of transmitted microwave intensity at 3.9 GHz for a cow leather with a sample size of 100 mm(length) x 100 mm (width) x 1.17 mm(thickness) and a basis weight of 860 g/m². The data are expressed in terms of the polar coordinates.

Figure 4.9 shows the angular dependence of ϵ' and ϵ'' at 3.9 GHz for the same sample used in Fig.4.8. The angular dependence also shows a pronounced anisotropy. The directions of the maximum ϵ' and ϵ'' deviate by about 83 degrees from the SD. The direction of the maximum ϵ'' corresponds to that of

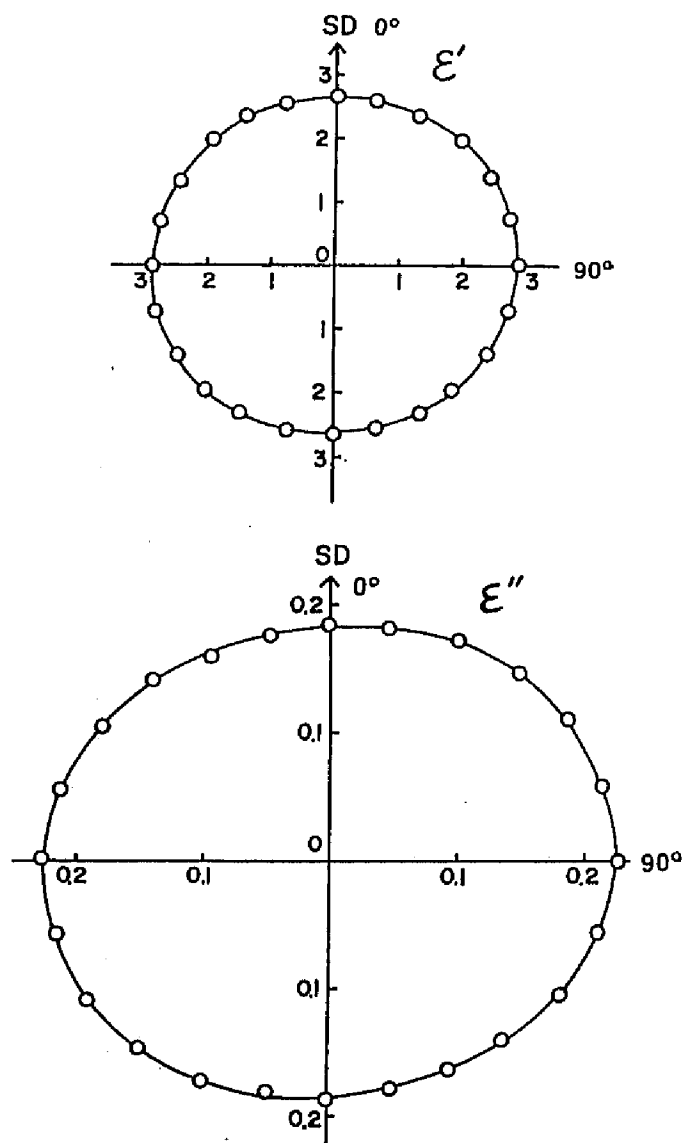


Fig.4.9 Angular dependence of ϵ' and ϵ'' at 3.9 GHz for the cow leather used in Fig.4.8. The data are expressed in terms of the polar coordinates.

minimum transmitted microwave intensity. The angular dependence of ϵ'' suggests that the change in dipole moment due to the reorientation of molecules is the largest in the direction of 83 degrees. The orientation pattern and the angular dependence of ϵ' and ϵ'' observed for the cow leather are similar to those obtained for anisotropic paper sheets.

The angular dependence of mechanical breaking strength for the cow leather with a thickness of 1.17 mm and a basis weight of 860 g/m² is shown in Fig.4.10. The direction of maximum mechanical breaking strength deviates by about 80 degrees from the SD and approximately coincides with that of the minimum transmitted microwaves. Thus, the collagen fibers should be mainly oriented in the direction of the maximum mechanical

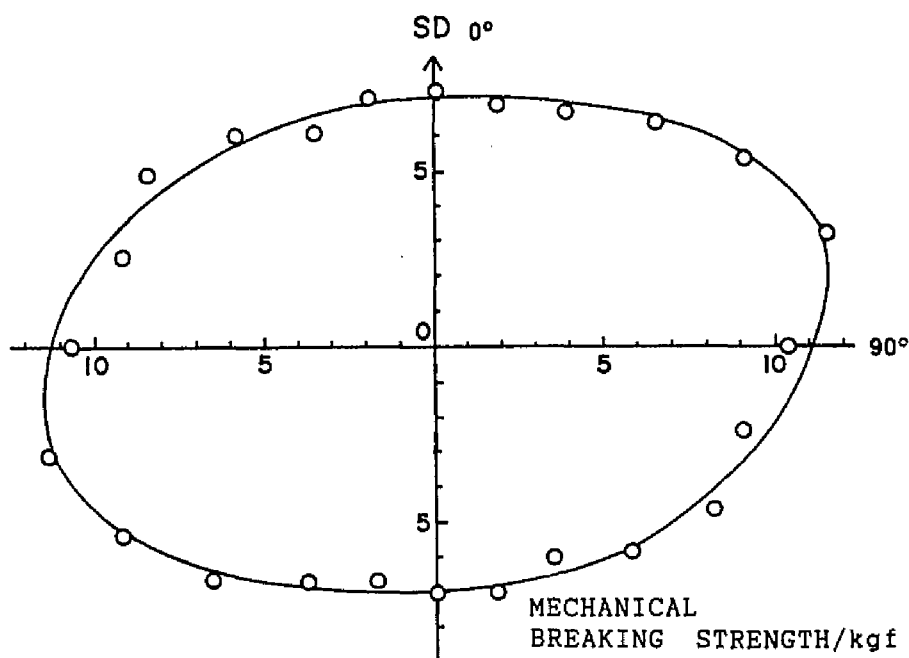
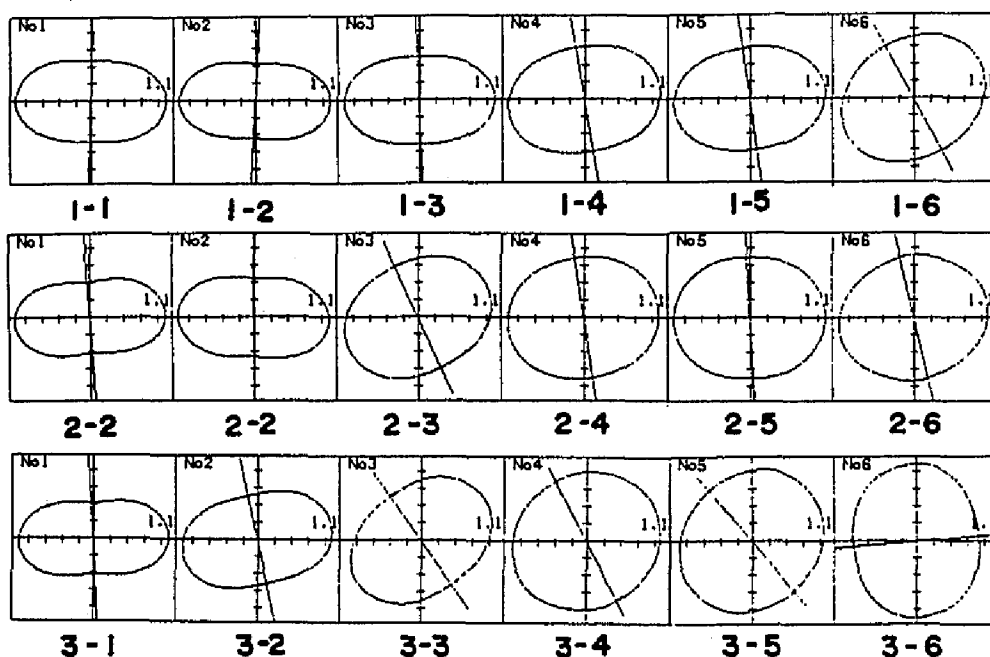


Fig.4.10 Angular dependence of mechanical breaking strength for the cow leather with 1.17 mm thickness and a basis weight of 860 g/m². The data are expressed in terms of the polar coordinates.

breaking strength or in the direction of the minimum transmitted microwaves.

Figure 4.11 shows the orientation patterns at different positions for the cow leather with a thickness of 1.15 mm and a basis weight of ca. 850 g/m². The specimens used here have been shown in Fig.4.1. The orientation patterns for the cow leather sheet varied remarkably with changing position, indicating that the orientation of fibers in the cow leather is not uniform at any positions. Actually, the orientation



ORIENTATION PATTERN (COW LEATHER)

$f = 4.0 \text{ GHz}$

Fig.4.11 Orientation patterns for the 18 specimens prepared at different positions of the cow leather with a size of 300 x 600 mm. The sample size and the basis weight were 100 mm x 100 mm x 1.15 mm and ca. 850 g/m², respectively.

angle θ and MOR also changed with changing position (see Figure 4.12). These findings imply that the main chain direction of the collagen fibers and the degree of orientation vary with changing position.

Figure 4.13 shows the angular dependence of ϵ'' at two different positions for the cow leather used in Fig. 4.11. The directions of maximum ϵ'' are similar to what we have seen in the orientation patterns of Fig. 4.11. The results in Figs. 4.11 to 4.13 suggest that the orientation of the collagen fibers should be different at different positions. Such a

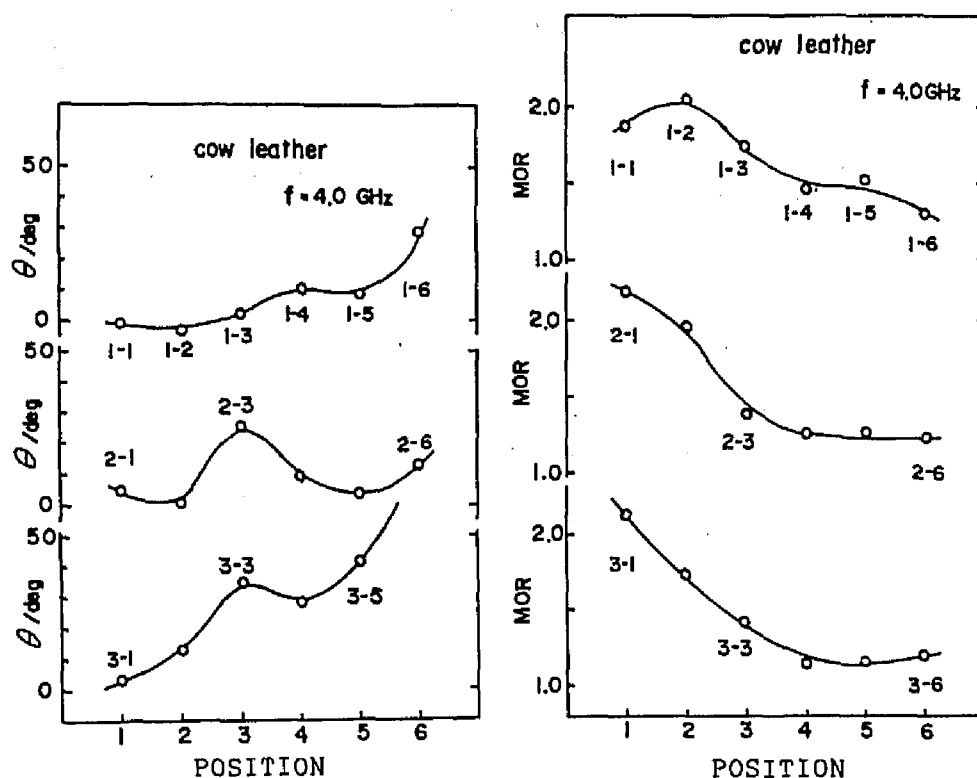


Fig. 4.12 Orientation angles θ and MOR values determined at 18 different positions of the cow leather with a size of 300 x 600 mm. The sample size and the basis weight were 100 mm x 100 mm x 1.15 mm and ca. 850 g/m², respectively.

difference in both orientation pattern and dielectric loss may be ascribed to varying textures of the cow leather.

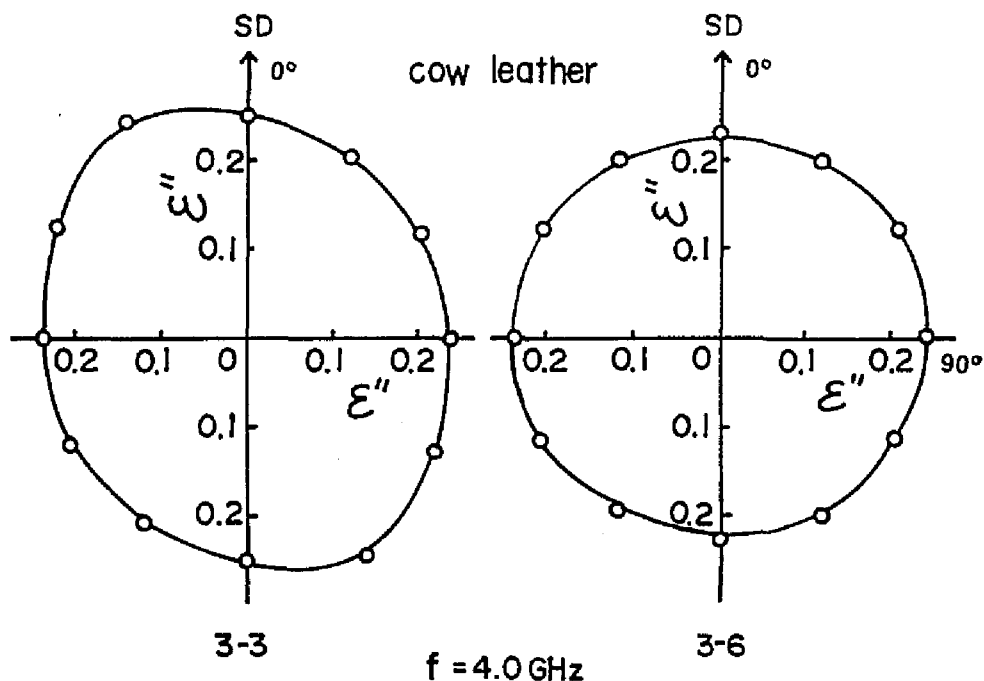


Fig.4.13 Angular dependence of ϵ'' at 4.0 GHz for the cow leather sheets cut at two different positions. The data are expressed in terms of the polar coordinates.

4.6 Discussion

Nonwoven Fabrics

The orientation pattern and the angular dependence of ϵ' and ϵ'' give information on physical properties of nonwoven fabrics in the CD. For our nonwoven fabrics consisting of rayon fibers, we may write the angle ϕ between the main axis of fibers and the MD as¹⁷

$$\langle \cos^2 \phi \rangle = \int_0^\pi \epsilon''(\phi) \cos^2 \phi d\phi / \int_0^\pi \epsilon''(\phi) d\phi \quad (4.6)$$

which becomes equal to 1 for a perfectly oriented film in the MD and becomes equal to 1/2 for a randomly oriented sample. Here, $\cos^2 \phi$ was used instead of $\sin^2 \phi$ because ϵ'' was the largest in the direction of the main chains for fibers. The values of $\epsilon''(\phi)$ may also be determined from the angular dependence of ϵ'' at a fixed frequency. In the case of two-dimensional distribution of fibers on the plane of fabrics, the orientation function may conveniently be used:

$$H = \{ 2 \langle \cos^2 \phi \rangle - 1 \} / 2 \quad (4.7)$$

where H is a fiber orientation function in the nonwoven fabric.

This function should be 1/2 for a perfectly oriented fabrics in the MD, while it is zero for a randomly oriented fabrics.

We determined the value of H to be 0.043 from the angular dependence of ϵ'' in Fig.4.2. This H value is relatively small, indicating that the fibers are oriented in a fixed direction, on the average. The quality control for the mechanical uniformity of fabrics can be determined by examining dielectric values and then changing machine conditions for the preparation of sheets. Thus, the use of the microwave method will improve the nonuniformity in quality along the CD.

It is not feasible to measure the thickness of nonwoven fabrics accurately by contact methods, because the fabrics consisting of fibers and voids are flexible and easily

compressed. The quality of nonwoven fabrics may be checked by measuring W of such fabrics instead of measuring thickness with a micrometer. However, since it takes a long time using the weight and volume of fabrics and to determine W , it is not so convenient.

Dielectric measurements at audio frequencies^{14, 18, 24} are not always effective for studying the physical properties of nonwoven fabrics, owing to the difficulty in making electrodes by evaporating metal. The evaporated metal penetrates into the fiber sheets with many voids. Using the microwave method, the fiber orientation can be determined accurately without contact, avoiding the problem inherent in dielectric measurements at audio frequencies.

Cow Leather

It follows from the equation of dielectric relaxation that ϵ'' is parallel to the number of dipoles of segment per unit volume.⁷ The angular dependence of ϵ'' reflects the distribution of protein molecules consisting of collagen fibers. Therefore, the fairly strong anisotropy in ϵ'' and the angular dependence of transmitted microwave intensity clearly shows that the collagen fibers constituting the cow leather should be oriented mainly a preferable direction. Since the change in dipole moment due to the reorientation of protein molecules is the largest in the direction of ca. 83 degrees, the protein molecules in collagen fibers may also be oriented in the preferable direction. The anisotropy found by our microwave method for the cow leather coincided with that in the mechanical breaking strength. The observed change in anisotropy with varying position may have something to do with

the function of the skin. For example, the expansion and the contraction corresponding to the movement of the cow body may require the preferable orientation of collagen fibers in a fixed direction.

The density of the cow leather used in the present study was determined to be about 0.735 g/cm^3 . This small value means that the cow leather contains many voids, as shown in Photo.4, and explains the small ϵ' and ϵ'' values obtained for the cow leather. The dielectric values may also be affected by the chemical composition and the content of water.

4.7 Conclusion

The angular dependences of transmitted microwave intensity, ϵ' and ϵ'' allows the fiber orientation to be accurately determined for nonwoven fabrics and cow leather sheets. The fiber orientation changed with changing positions of the sheets. This microwave method is quite promising for evaluating the physical properties of sheet materials with voids.

CONCLUSIONS

This thesis has dealt with the following subject: findings of a new method and a new type of instrument for accurately determining the fiber orientation of sheet materials such as paper, nonwoven fabrics and cow leather by use of polarized microwaves. Emphasis was put on the determination of an orientation pattern reflecting the orientational distribution of fibers in sheets. The principal results are as follows:

(1) A new method and a new type of instrument was developed for accurately determining the fiber orientation from the dielectric anisotropy by use of microwaves. The instrument consists of a pair of rectangular waveguides with a narrow gap in which the sample sheet is set. The polarized microwaves are irradiated vertically to the sheet, which is rotated for 6.0 s around the central axis normal to the sheet plane. The angular dependence of the transmitted microwaves and complex dielectric constant leads to the determination of the fiber orientation. Thus, the new method allows the orientation angle, the ratio MOR of maximum to minimum intensity of the transmitted microwaves, the ratio of CD to MD transmitted microwave intensity, the measuring frequency, and the complex dielectric constant at microwave frequencies to be determined in as short a time as 30 s.

(2) The new method using microwaves makes it possible to determine the fiber orientation of paper nondestructively. Based on results obtained by the mechanical breaking strength and infrared absorption measurements, the direction of the molecular orientation of cellulose chains is reflected in the orientation angle determined by the microwave method. A

correlation coefficient of 0.92 was obtained between the orientation angles determined from the angular dependences of the mechanical breaking strength and of microwave attenuation. The analyzer is useful for a quick determination of orientation in various papers.

(3) The new type of method using microwaves determines the dielectric anisotropy and refractive index for optically opaque paper sheets. The dielectric anisotropy ascribable to the local motions of cellulose molecules is supported by electron microscopic observations and mechanical anisotropy. The angular dependence of the complex dielectric constant gives the degree of molecular or fiber orientation and the distribution of cellulose molecules in paper sheets. The direction of the average orientation of molecular chains can be inferred from the anisotropic data. In order to study the effect of density of paper sheets with voids, the ϵ' and ϵ'' at microwave frequencies are determined for handsheets of various densities prepared by changing freeness, mesh size for fractionation and pressure for wet pressing. The accumulation of data for complex dielectric constant and refractive index at microwave frequencies gives an important chart for manufacturing the functional paper corresponding to needs.

(4) The new method uses polarized microwaves to determine the fiber orientation of nonwoven fabric and cow leather sheets without contact and destruction. The angular dependence of transmitted microwave intensity at 4.0 GHz allows the fiber orientation to be determined in only 30 s. The molecular orientation ratio and the orientation angle changed with changing position of nonwoven fabric and cow leather sheets. An orientation function was estimated from the angular

dependence of ϵ'' as a measure of the distribution of fibers in the nonwoven fabric. The resonance frequency can be used to estimate the variation in basis weight in the cross machine direction. The direction of the minimum transmitted microwave intensity and the maximum dielectric loss coincides with that of the maximum mechanical breaking strength, suggesting that the polyester fibers in the nonwoven fabrics and the collagen fibers in the cow leather should be oriented mainly in a preferred direction of the maximum transmitted microwaves and the maximum dielectric loss. The present microwave method was found to be convenient for determining the orientation of fibers in nonwoven fabric and cow leather sheets accurately, nondestructively and without contact.

Finally, the new type of microwave method developed by the author made clear the fiber orientation of the sheet materials such as paper, nonwoven fabrics and cow leather and then will occupy an indispensable position for studying the physical properties such as the fiber orientation and the dielectric anisotropy at microwave frequencies. The present microwave gives a new tool for quickly determining the molecular or fiber orientation of sheet materials without contact instead of the conventional methods such as X-ray diffraction, infrared absorption, ultrasonic velocity, mechanical breaking strength, etc.

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APPENDIX

A.1 Dielectric Anisotropic Index

According to eqs.(1.4) and (1.5), ϵ' and ϵ'' decrease with increase in t , which is an increasing function of the content of voids in the sheet if the basis weight stays unchanged.

If the fiber arrangement and the basis weight are the same for two sheets with different thicknesses $t(1)$ and $t(2)$, the resonance frequency and Q value observed for them do not differ. For these sheets eqs.(1.4) and (1.5) give

$$[\epsilon'(1)-1]/[\epsilon'(2)-1] = t(2)/t(1) \quad (A-1)$$

$$\epsilon''(1)/\epsilon''(2) = t(2)/t(1) \quad (A-2)$$

which indicate that the ratios of $[\epsilon'(1)-1]/[\epsilon'(2)-1]$ and $\epsilon''(1)/\epsilon''(2)$ depend only $t(2)/t(1)$. Here, $\epsilon'(1)$, $\epsilon''(1)$ and $\epsilon'(2)$, $\epsilon''(2)$ are the values in a fixed direction for the samples with thicknesses of $t(1)$ and $t(2)$, respectively.

The direction of maximum ϵ' or ϵ'' may not differ for the two samples. Thus, eqs.(A-1) and (A-2) yield

$$[\epsilon'_{max}(1)-1]/[\epsilon'_{min}(1)-1] = [\epsilon'_{max}(2)-1]/[\epsilon'_{min}(2)-1] \quad (A-3)$$

$$\epsilon''_{max}(1)/\epsilon''_{min}(1) = \epsilon''_{max}(2)/\epsilon''_{min}(2) \quad (A-4)$$

which imply that both $\epsilon''_{max}/\epsilon''_{min}$ and $(\epsilon'_{max}-1)/(\epsilon'_{min}-1)$ are invariant for samples with different thicknesses but the

same basis weight. In other words, these ratios should give an anisotropic index essentially free from the effect of voids.

More generally, the following relations can be derived for a given sample:

$$(\epsilon'_{max} - 1) / (\epsilon'_{min} - 1) = (f_{1r} - f_{2r(max)}) / (f_{1r} - f_{2r(min)})$$

(A-5)

$$\epsilon''_{max} / \epsilon''_{min} = (1/Q_{2(max)} - 1/Q_1) / (1/Q_{2(min)} - 1/Q_1) \quad (A-6)$$

These ratios of $(\epsilon'_{max} - 1) / (\epsilon'_{min} - 1)$ and $\epsilon''_{max} / \epsilon''_{min}$ may be considered to be anisotropic indices substantially free from the effects of voids.

A.2 Dielectric Relaxation

For the dielectric relaxation (β -relaxation) due to local motion of macromolecules, the dielectric strength $\epsilon'_0 - \epsilon'_\infty$ can be written as⁵⁰

$$\epsilon'_0 - \epsilon'_\infty = (4\pi/3) (N\mu^2/\xi) (F_r/F) \quad (A-7)$$

where ϵ'_0 is the dielectric constant at low frequencies, ϵ'_∞ is the dielectric constant at high frequencies, N is the number of dipoles per unit volume, μ is the dipole moment, ξ is the restoring force, F_r is the local electric field, and F is the applied electric field. From (A-7) we express the dielectric constant $\epsilon'(\omega)$ and dielectric loss $\epsilon''(\omega)$ for the dielectric β -relaxation as

$$\epsilon'(\omega) - \epsilon'_\infty$$

$$= (4\pi/3) (N\mu^2/\xi) \int [g(\tau_1)/(1+(\omega\tau_1)^2)] (F_r/F) \propto N \propto \rho$$

(A-8)

$$\epsilon''(\omega)$$

$$= (4\pi/3) (N\mu^2/\xi) \int [g(\tau_1)\omega\tau_1/(1+(\omega\tau_1)^2)] (F_r/F) \propto N \propto \rho$$

(A-9)

which indicate that $\epsilon'(\omega) - \epsilon'_\infty$ and $\epsilon''(\omega)$ at an angular frequency of ω are linearly related to N . Here, g is the relaxation spectrum and τ is the relaxation time. Since N is proportional to the density ρ , both $\epsilon'(\omega) - \epsilon'_\infty$ and $\epsilon''(\omega)$ at a fixed microwave frequency should vary in proportion to the density ρ of a paper sheet.

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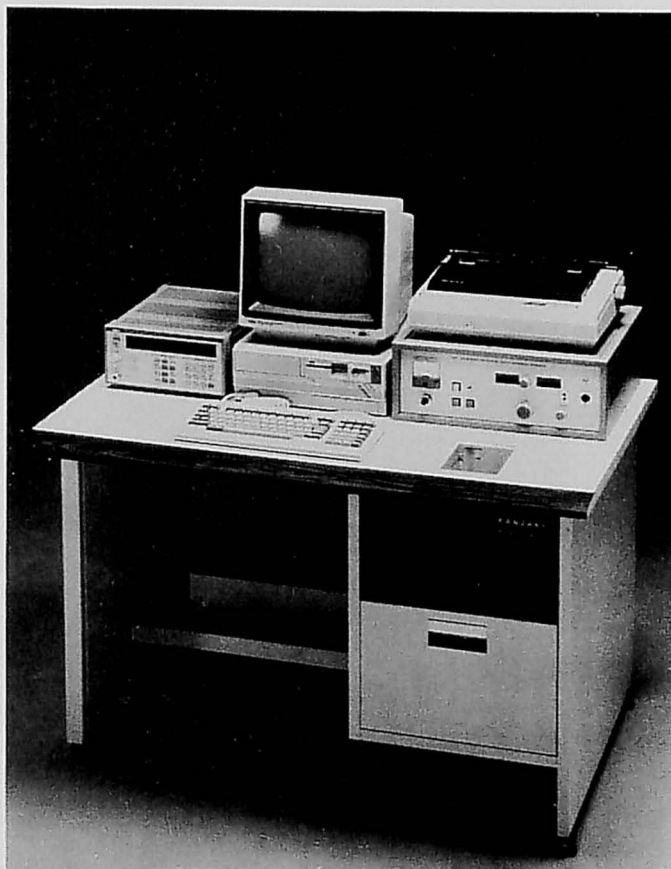


Photo.1 Microwave molecular orientation analyzer.

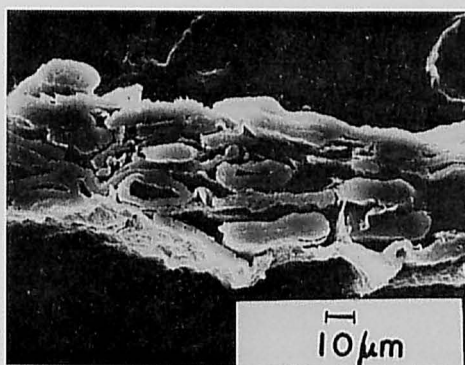
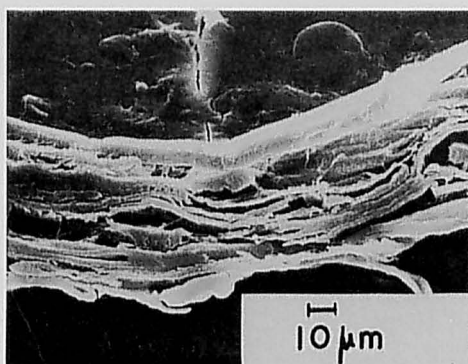
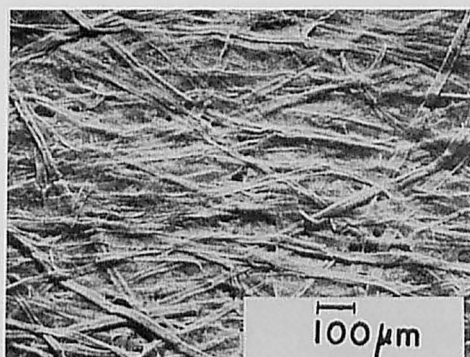


Photo.2 Electron microphotographs of the surface and the cross sections in the MD and CD for a uniaxially oriented paper with a thickness of $85 \mu\text{m}$ and a basis weight of 41 g/m^2 .

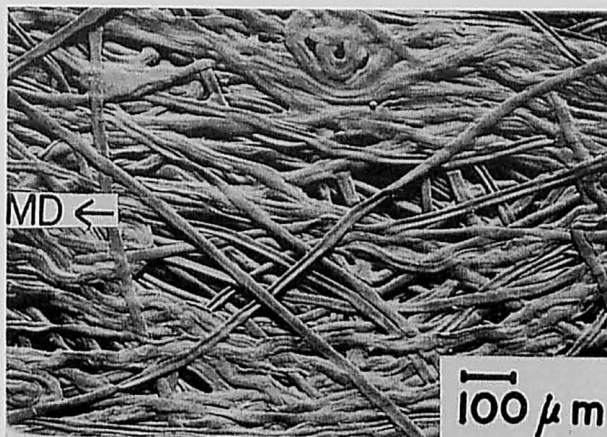


Photo.3 Electron microphotograph for the surface of the nonwoven fabric (43 g/m^2).

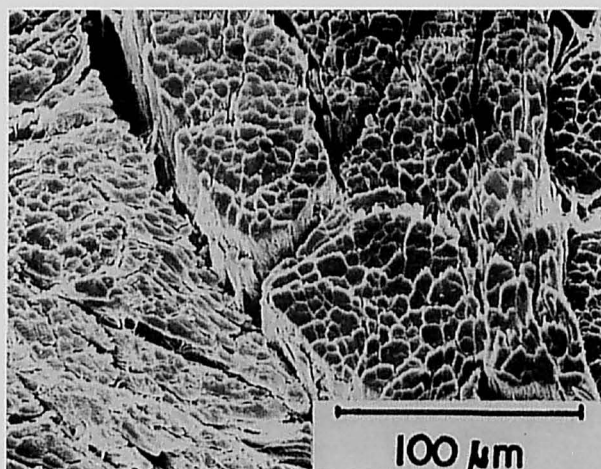


Photo.4. Electron microphotograph of a cross section of the cow leather.